A SYSTEMATIC HANDBOOK

OF

VOLUMETRIC ANALYSIS

A SYSTEMATIC HANDBOOK OF

VOLUMETRIC ANALYSIS

OR

THE QUANTITATIVE DETERMINATION
OF CHEMICAL SUBSTANCES BY MEASURE, APPLIED
TO LIQUIDS, SOLIDS, AND GASES.

ADAPTED TO THE REQUIREMENTS OF PURE CHEMICAL RESEARCH,
PATHOLOGICAL CHEMISTRY, PHARMACY, METALLURGY, MANUFACTURING
CHEMISTRY, PHOTOGRAPHY, ETC., AND FOR THE VALUATION
OF SUBSTANCES USED IN COMMERCE, AGRICULTURE, AND THE ARTS.

BY

FRANCIS SUTTON, F.I.C., F.C.S.

ELEVENTH EDITION

REVISED THROUGHOUT, WITH NUMEROUS ADDITIONS, BY

W. LINCOLNE SUTTON, F.I.C.

PUBLIC ANALYST FOR THE COUNTIES OF NORFOLK AND SUFFOLK, NORWICH, IPSWICH, ETC.,
ENGLAND

AND

ALFRED E. JOHNSON, B.Sc. LOND., F.I.C., A.R.C.Sc.I.

ADDITIONAL PUBLIC ANALYST FOR THE COUNTY OF STAFFORD AND THE BOROUGH OF
WOLVERHAMPTON, ETC., ENGLAND

LONDON
J. & A. CHURCHILL
7 GREAT MARLBOROUGH STREET, W. 1
1924
Printed in Great Britain

First Edition	1863
Second ,, ...	1871
Third ,, ...	1876
Fourth ,, ...	1882
Fifth ,, ...	1886
Sixth ,, ...	1890
Seventh ,, ...	1896
Eighth ,, ...	1900
Ninth . . .	1904
Tenth ,, ...	1911
Eleventh ,, ...	1921

French Edition, translated by Dr C. Mehu (Masson, Paris), 1885

PREFACE.

THE last (tenth) edition of this book, and the first edited by us, was published as long ago as 1911, when Mr. Francis Sutton was still living at the age of eighty and able to sign the Preface. In this preface he expressed the hope that he would live to see the Jubilee (1863-1913) of "the least perishable work, I suppose, of my life." This hope was fulfilled (he died in 1917 aged 86), but he did not survive to see a further edition, which perhaps he might have seen but for the War.

Unfortunately, from various causes the publication of this edition has been greatly delayed, and the book has been out of print for several years. Considerable changes have now been made, which, it is hoped, will be found to add to its usefulness. Whereas previously it was usual to print all the "Methods of Procedure" in smaller type than the other portions of the text, we have throughout this edition adopted almost uniformly a large and clear type.

The section on Gas Analysis in previous editions was mainly the work of Dr. Herbert McLeod, F.R.S., who died at an advanced age whilst this book was passing through the press. This section having become very much out-of-date, the services of Messrs. H. Hollings, M.Sc., and J. S. G. Thomas, D.Sc., two well-known specialists, were secured, and they have contributed an entirely new section, which constitutes a comprehensive and up-to-date little treatise on the subject such as has not previously existed in English.

The whole work has been carefully revised throughout, and many additions and replacements made. In Parts I. and II. the sections on the burette, pipette and graduated flask have been entirely re-written, and full details given of the methods of standardisation employed at the National Physical Laboratory, with the "limits of error" allowed. The section on Indicators has also been entirely re-written, with many additions. The most recent methods for the technical analysis of ammoniacal liquors have again been included. The description of the Kjeldahl process has been re-written, with additions. Several alterations and additions have been made in Parts III. and IV. In Parts V. and VI. the alterations and additions are far too numerous to specify, whilst several portions have been re-written. In the metallurgical sections we desire to acknowledge particularly the valuable assistance rendered by Mr. Bernard Collitt, F.I.C. In Part VI., under "Glycerin," the International Methods of Analysis are given in full. Bloxam's methods of determining Indigo are fully described. The section on Sugars and Starch has been thoroughly revised. Under "Tannins" the most recent methods of analysis are given.

The Water and Sewage Analysis section has again been thoroughly revised, with several additions, especially in the portion dealing with the determination of Dissolved Oxygen. For Table IX., "Dissolved Oxygen in Natural Waters" under stated conditions of temperature and salinity we are indebted to Dr. E. C. Jee, Technical Adviser to the Standing Committee on Rivers Pollution (1921) Ministry of Agriculture and Fisheries. The Table is founded upon the values determined by Dr. C. J. J. Fox (*Publications de Circonstance No.* 41). A new feature in this edition is the collection of typical analyses of the public water supplies of Great Britain. Several public analysts have kindly made special analyses for this purpose, or have supplied information not to be obtained elsewhere. The description of Sir E. Frankland's combustion method of analysing water residues has been deleted on the ground of being very little used for years past.

The International Atomic Weights for 1923 have been adopted throughout, and all factors, numerical examples, etc., re-calculated where necessary. Many of the original papers summarised in the book have been re-read and fuller extracts given. Throughout the work we have endeavoured in all cases to give the important working details which count for so much in the practical work of the laboratory.

THE EDITORS.

TABLE OF CONTENTS.

PAGE
MEMORANDA xi

PART I.

GENERAL PRINCIPLES 1
The Balance 4
Technical terms 5
Volumetric Analysis without Weights . . . 6
Volumetric Analysis without Burettes . . . 7
The Burette 8
On the Correct Reading of Burettes 13
The Pipette 15
The Measuring Flask 16
The Calibration of Graduated Apparatus 18
Weights and Measures used in Volumetric Analysis 24
Normal Solutions 29

PART II.

ALKALIMETRY AND ACIDIMETRY 32
Indicators 32
Theory of Indicators 41
Preparation of Normal Acid and Alkali Solutions . . . 45
Adjustment of Standard Solutions 56
Titration of Alkali Salts 59
Direct Determination of Sodium 65
Technical Analysis of Alkali Compounds 69
Titration of Alkaline Earths and their Compounds . . . 73
Ammonia 75
Analysis of Ammoniacal Liquors 79
Kjeldahl's Method 85
Acetic Acid 93
Boric Acid and Borates 97
Carbonic Acid and Carbonates 101
Citric Acid 114
Formic Acid 115
Hydrofluoric and Hydrofluosilicic Acids 116
Oxalic Acid 120
Phosphoric Acid 120
Fuming Sulphuric Acid 122
Tartaric Acid 123

PART III.

ANALYSIS BY OXIDATION OR REDUCTION 127
Potassium Permanganate and Ferrous Salts 128
Potassium Dichromate and Ferrous Salts 132
Iodimetry and Iodimetric Processes 134
Use of Potassium Iodate in Iodimetry 138
Analysis of Substances by Distillation with Hydrochloric Acid . . . 140
Arsenious Acid and Iodine 144

PART IV.

PAGE

ANALYSIS BY PRECIPITATION 146
- Determination of Chlorine by Silver Solution 146
- Indirect Analyses by Decinormal Silver and Potassium Chromate . . 149
- Determination of Silver in Acid Solution 150

PART V.

APPLIED METHODS OF ANALYSIS.—INORGANIC SUBSTANCES . . . . .

- Aluminium 153
- Antimony 156
- Arsenic 161
- Barium 172
- Bismuth 173
- Bromine 176
- Cadmium 179
- Calcium 180
- Cerium 181
- Chlorine 183
- Chlorine Gas and Bleach 185
- Chromium 192
- Cobalt 200
- Copper 201
- Cyanogen 218
- Ferro- and Ferri-cyanides 220
- Thiocyanates 226
- Gold 228
- Iodine 229
- Iron (Ferrous) 236
- Iron (Ferric) 240
- Iron Ores, Iron and Steel 246
- Lead 252
- Magnesium 258
- Manganese 260
- Mercury 273
- Nickel 278
- Nitrates and Nitrites 285
- Nitrites 300
- Dissolved Oxygen (see Part VIII., p. 468) 304
- Hydrogen Peroxide 304
- Sodium Peroxide and Perborate 306
- Phosphoric Acid and Phosphates 307
- Selenium 318
- Silver 318
- Sulphur, Sulphides and Sulphites 324
- Sulphuretted Hydrogen 334
- Sulphuric Acid and Sulphates 336
- Persulphates 342
- Tin 343
- Titanium 348
- Uranium 350
- Vanadium 351
- Zinc 353

PART VI.

APPLIED METHODS OF ANALYSIS.—ORGANIC SUBSTANCES . . . . .

- Acetone 364
- Aniline 365
- Azo-Dyes, Nitro- and Nitroso-Compounds 367
- Carbon Disulphide and Thiocarbonates 369
- Formaldehyde 371

PAGE
Glycerol . . . 375
Indigo . . . 383
Oils, Fats and Waxes . . . 387
Butter . . . 391
Phenol . . . 404
Salicylic Acid . . . 406
Sugars . . . 409
Starch . . . 417
Tannins . . . 418

PART VII.

ANALYSIS OF URINE . . . 428

PART VIII.

ANALYSIS OF WATER AND SEWAGE . . . 444
Special Index to the Analytical Processes . . . 444

PART IX.

VOLUMETRIC ANALYSIS OF GAS . . . 499
Methods of Sampling . . . 499
Preparation of Absorption and Eudiometric Tubes . . . 510
Correction of Volume of Gas . . . 520
Methods of Analysis . . . 529
Direct Determination by Absorption . . . 530
Indirect Determination . . . 534
Fractional Combustion . . . 541
Forms of Apparatus . . . 550
Simpler Methods and Apparatus . . . 564
Calculation of Calorific Value . . . 572
Determination of Gases by Titration . . . 573
Micro-Gas Analysis . . . 582
The Nitrometer . . . 590
Index to Part IX. . . . 599
TABLES . . . 603
ADDENDA and CORRIGENDA . . . 622
INDEX TO PARTS I.–VIII. . . . 625

LIST OF TABLES.

International Atomic Weights, 1923, abridged . . . xii
Correction of Volumes of Liquids for Temperature . . . 28
Thomson's Classification of Indicators . . . 40
Strength of Sulphuric Acid by Sp. Gr. . . . 52
Normal Factors for Alkalis, Alkaline Earths and Acids . . . 59
Organic Salts of Alkalis: Factors for Titration of residue left after ignition . 69
The amount of Ammonium Sulphate produced by Gas Liquor . . . 79
Factors for use in Analysis of Ammoniacal Liquors . . . 85
Factors for use with Decinormal Potassium Permanganate . . . 132
Saponification or Kottstorfer Value of Oils and Fats . . . 390
Determination of Sugars by Fehling's Solution . . . 414
Tannin in various Substances . . . 422
Analyses of Sewage Effluents . . . 486
Typical Analyses of Water . . . *facing* 499
Tables for Gas Analysis . . . 604 *et seq.*
Tables for Water Analysis . . . 612 *et seq.*
TABLE OF FACTORS AND THEIR LOGARITHMS FOR VOLUMETRIC ANALYSIS . 618

MEMORANDA.

WEIGHTS AND MEASURES.

(See p. 24.)

1 metre = 39·370113 inches.
" = 3·280843 feet.
1 gram (gm.) = 15·432356 grains (grs.).
1 kilogram = 2·2046 lb.

The standard litre is the volume of a kilogram of pure water at 4° C. under standard barometric pressure.

1 litre = 1000·027 cubic centimetres.
" = 1·75980 pints.
" = 0·2200 gallon.

1 litre of water at 15° C. and 760 mm. weighs 998·05 grams. (See p. 27.)

TEMPERATURE.

The usual standard temperature for graduated vessels and standard solutions used in volumetric analysis is 15° C. (= 59° F.). For special purposes, however, other temperatures are also in common use (see p. 26).

NORMAL SOLUTIONS.

A normal solution of a reagent is one that contains in a litre that proportion of its molecular weight in grams which corresponds to 1·008 gram of available hydrogen or its equivalent (see p. 29). Decinormal ($^N/_{10}$) and centinormal ($^N/_{100}$) solutions are respectively of one-tenth and one-hundredth of this strength.

By means of a standard solution, a given volume of which has been proved to be equivalent to a known amount of a certain substance, the quantity of such substance contained in a given quantity of another solid or liquid body can be determined. This process is termed *titration* (see p. 4).

ABBREVIATIONS USED.

Ber. = Berichte der deutschen chemischen Gesellschaft.
C. N. = Chemical News.
J. A. C. S. = Journal of the American Chemical Society.
J. C. S. = Journal of the Chemical Society.
J. S. C. I. = Journal of the Society of Chemical Industry.
Z. a. C. = Zeitschrift für analytische Chemie.
Z. f. angew. C. = ,, ,, angewandte ,,

ABRIDGED LIST OF THE INTERNATIONAL ATOMIC WEIGHTS FOR 1923

(used throughout this work).

		O = 16.			O = 16.
Aluminium	Al	27·1	Magnesium	Mg	24·32
Antimony	Sb	120·2	Manganese	Mn	54·93
Arsenic	As	74·96	Mercury	Hg	200·6
Barium	Ba	137·37	Molybdenum	Mo	96
Bismuth	Bi	208	Nickel	Ni	58·68
Boron	B	10·9	[1] Nitrogen	N	14·01
Bromine	Br	79·92	Oxygen	O	16
Cadmium	Cd	112·4	Palladium	Pd	106·7
Calcium	Ca	40·07	Phosphorus	P	31·04
[1] Carbon	C	12	Platinum	Pt	195·2
Cerium	Ce	140·25	Potassium	K	39·1
Chlorine	Cl	35·46	Silicon	Si	28·3
Chromium	Cr	52	Silver	Ag	107·88
Cobalt	Co	58·97	Sodium	Na	23
Copper	Cu	63·57	Strontium	Sr	87·63
Fluorine	F	19	Sulphur	S	32·06
Gold	Au	197·2	Tin	Sn	118·7
Hydrogen	H	1·008	Titanium	Ti	48·1
Iodine	I	126·92	Tungsten	W	184
Iron	Fe	55·84	Uranium	U	238·2
Lead	Pb	207·2	Vanadium	V	51
Lithium	Li	6·94	Zinc	Zn	65·37

[1] These values for Carbon and Nitrogen have been retained in order to avoid unnecessary recalculations. The latest values are 12·005 and 14·008 respectively.

VOLUMETRIC ANALYSIS

OF

LIQUIDS AND SOLIDS.

PART I.

GENERAL PRINCIPLES.

QUANTITATIVE analysis by weight, or gravimetric analysis, consists in separating out the constituents of any compound, either in a pure state or in the form of some new substance of known composition, and accurately weighing the products. Such operations are frequently very complicated, and occupy a long time, besides requiring in many cases elaborate apparatus, and the exercise of much care and experimental knowledge. Volumetric processes on the other hand, are, as a rule, quickly performed; in most cases are susceptible of extreme accuracy, and need much simpler apparatus. The leading principle of the method consists in submitting the substance to be determined to certain characteristic reactions, employing for such reactions solutions of known strength, and from the volume of solution necessary for the production of such reaction calculating the weight of the substance to be determined by aid of the known laws of chemical equivalence.

Volumetric analysis, or quantitative chemical analysis by measure, in the case of liquids and solids, consequently depends upon the following conditions for its successful practice:—

1. A solution of the reagent, the chemical value of which is accurately known, called the "standard solution".

2. A graduated vessel from which portions of it may be accurately delivered, called the "burette".

3. The decomposition produced by the standard solution with any given substance must either in itself or by an indicator be such, that *its termination is unmistakable to the eye*, and thereby the quantity of the substance with which it has combined accurately calculated.

Suppose, for instance, that it is desired to know the quantity of pure silver contained in a shilling. The coin is first dissolved in nitric acid, by which means a bluish solution, containing silver, copper, and probably other metals, is obtained. It is a known fact that chlorine combines with silver in the presence of other metals to form silver chloride, which is insoluble in nitric acid. The proportions in which the combination takes place are 35·46 of chlorine to every 107·88 of silver. Consequently if a standard solution of sodium chloride is made by dissolving 58·46 gm. of the pure salt (equivalent to 35·46 gm. of chlorine) in water and diluting to 1000 c.c., each c.c. of this solution will combine with 107·88/1000 = 0·10788 gm. of pure silver to form silver chloride as a white curdy precipitate which settles rapidly, especially on stirring, leaving a clear supernatant liquid above. The above standard solution is run carefully from a vessel graduated in cubic centimetres, while stirring the liquid, until a point is at length reached when the addition of one more drop of the standard sodium chloride solution fails to produce the least opalescence in the liquid. This shows that the whole of the silver has been precipitated from the solution. The number of cubic centimetres thus added is then noted and would be about 48·4 in the case of a new shilling. Hence 48·4 × 0·10788 = 5·221 gm. silver, equivalent to 80·6 grains, is the amount present in the coin.

This method of determining the quantity of silver in any given solution occupies scarcely a quarter of an hour, whereas the determination by weighing could not be done in half a day, and even then not so accurately as by the volumetric method. It must be understood that there are certain necessary precautions in conducting the above process which have not been described; those will be found in their proper place; but from this example it will at once be seen that the saving of time and trouble, as compared with the older methods of analysis, is immense; besides which, in the majority of instances in which it can be applied, it is equally accurate, and in many cases much more so.

The only conditions on which the volumetric system of analysis can be carried on successfully are great care with respect to the graduation of the measuring instruments, and their agreement with each other, the strength and purity of the standard solutions, and the absence of other matters which would interfere with the accurate determination of the particular substance sought.

The fundamental distinction between gravimetric and volumetric analysis is that, in the former method, the substance to be determined must be completely isolated in the purest possible state or combination, necessitating in many instances very patient and discriminating labour; whereas, in volumetric processes, such complete separation is very seldom required, the processes being so contrived as to admit of the presence of half a dozen or more other substances which have no effect upon the particular chemical reaction required.

The process just described for instance, the determination of silver in coin, is a case in point. The alloy consists of silver and copper, with small proportions of lead, antimony, tin, etc. None of these metals affect the amount of salt solution which is chemically required to precipitate the silver, whereas, if the metal had to be determined by weight, it would be necessary first to filter the nitric acid solution to free it from insoluble tin, etc.; then precipitate with a slight excess of sodium chloride; then bring the precipitate upon a filter, and wash repeatedly with pure water until every trace of copper, salt, etc., is removed. The pure silver chloride is then carefully dried, ignited separately from the filter, and weighed; the filter burnt, the residue as reduced metallic silver and filter ash allowed for, and thus finally the amount of silver is found by the balance with ordinary weights.

On the other hand, the volumetric process has been purely chemical, the burette or measuring instrument has taken the place of the balance, and theoretical or atomic weights have supplanted ordinary weights.

The end of the operation in this method of analysis is in all cases made apparent to the eye. In alkalimetry it is the change of colour produced in litmus, turmeric, or other sensitive colouring matter; the formation of a permanent precipitate, as in the determination of cyanogen; a precipitate ceasing to form, as in chlorine and silver determination; the appearance of a distinct colour, as in iron analysis by permanganate solution, and so on.

I have adopted the classification of methods used by **Mohr** and others, namely:—

1. **Methods of Saturation.**—Where the determination of the substance is effected by saturation with another substance of opposite properties,—generally understood to include acids and alkalis and alkaline earths.

2. **Methods of Oxidation and Reduction.**—Where the determination of a substance is effected by a reducing or oxidizing agent of known power, including most metals, with their oxides and salts. The principal oxidizing agents are potassium permanganate, potassium dichromate, and iodine; and the corresponding reducing agents, ferrous and stannous compounds, and sodium thiosulphate.

3. **Methods of Precipitation.**—Where the determination of a substance is effected by precipitating it in some insoluble and definite combination, an example of which occurs in the determination of silver described above.

This classification does not completely include all the volumetric processes that may be used, but it divides them into convenient sections for describing the peculiarity of the reagents used, and their preparation. If strictly followed out, it would in some cases necessitate the registration of the body to be determined under two or three heads. Copper, for instance, can be determined residually by permanganate; it can also be determined by precipitation with sodium sulphide. The determination of the same metal by potassium cyanide, on the other hand, would not come under any of the above heads.

It will be found, therefore, that liberties have been taken with the arrangement; and for convenient reference all analytical processes applicable to a given body are included under its name.

It may be a matter of surprise to some that several distinct volumetric methods for one and the same substance are given; but a little consideration will show that in many instances greater convenience, and also accuracy, may be gained in this way. The operator may not have one particular reagent at command, or he may have to deal with such a mixture of substances as to preclude the use of some one method; whereas another method may be quite free from such objection. The choice in such cases, of course, requires judgment, and it is of the greatest importance that the operator should be acquainted with the qualitative composition of the matters with which he is dealing, and that he should ask himself at every step why such and such a thing is to be done.

It will be apparent from the foregoing description of the volumetric system, that it may be successfully used in many instances by those who have never been thoroughly trained as analytical chemists; but we can never look for the scientific development of the system to such as these.

In the preparation of this work an endeavour has been made to describe all the operations and chemical reactions as simply as possible, all the necessary calculations being made as far as possible without the aid of long mathematical formulæ and requiring usually nothing further than a knowledge of the ordinary rules of arithmetic and occasionally of elementary algebra.

TECHNICAL TERMS.

THE following are the technical terms used in volumetric analysis, with their meanings:—

Titration is the process of determining the quantity of a certain substance in a solution by means of a reaction between that substance and a standard solution each c.c. of which is equivalent to a known weight of the substance to be determined.

This is **direct titration**.

The valuable process of **indirect titration** is used where the above is inapplicable, and the element, etc., to be determined has to be deduced from the titration of a decomposition product of a given liquid or solid substance. This is exemplified in the analysis of manganese ores, which by boiling with hydrochloric acid evolve chlorine. The latter is absorbed and determined, and the corresponding amount of manganese dioxide obtained by calculation.

Residual titration is the process of determining the quantity of a certain substance in a solution by first adding to it a measured volume of a standard solution more than sufficient to bring about a known chemical change, then determining the excess of the reagent thus added by means of another standard solution.

For example, native calcium or barium carbonate cannot be titrated directly with acid, because it is necessary to add hydrochloric (or nitric) acid in excess in order to effect solution. Hence, the method of procedure in this case is to weigh out, say, 0·25 gm. of the powdered mineral into a flask and to add water and a known volume (A c.c.) of standard hydrochloric acid, more than sufficient to decompose the carbonate. The flask is then heated gently till effervescence ceases and all is dissolved except some siliceous residue. After cooling, an indicator is added and a standard alkali solution, of equivalent strength to the standard acid, is carefully added from a burette until the liquid becomes neutral. Suppose that B c.c. are required. Then the combined acid is given by the difference A − B, whence the carbonate can be calculated, e.g. from the equation

$$BaCO_3 + 2HCl = BaCl_2 + CO_2 + H_2O.$$

Normal Solutions.—The definition of the term "normal solution" and full particulars as to the preparation and use of these are given on p. 29 *et seq.*

THE INSTRUMENTS AND APPARATUS.

THE BALANCE.

Strictly speaking, it is necessary to have two balances in order to carry out completely the volumetric system. One to carry about a kilogram in each pan and to turn when fully loaded with about 5 milligrams; the other to carry about 50 grams and to turn easily and quickly, when fully loaded, with one- or two-tenths of a milligram. The former instrument is used for weighing large amounts of pure reagents in the preparation of standard solutions, and for making the necessary weighings when graduating or testing measuring flasks. The latter instrument, which must be of much lighter construction, serves for weighing small quantities of substances to be tested, many of which, being hygroscopic, need weighing quickly as well as accurately, also for the delicate weighings required when testing the accuracy of pipettes and burettes.

For all technical purposes, however, a moderate-sized balance of medium delicacy is quite sufficient, especially if rather large quantities of substances are weighed and brought into solution,—then further subdivided by means of measuring flasks and pipettes.

The operator also requires, besides the balance and graduated instruments, beakers, porcelain basins, flasks, funnels, stirring rods, etc., as in gravimetric analysis. Above all, he must be practically familiar with proper methods of filtration, washing of precipitates, and the application of heat.

VOLUMETRIC ANALYSIS WITHOUT WEIGHTS.

This is more a matter of curiosity than of value; but, nevertheless, one can imagine circumstances in which it might be useful. In carrying it out, it is necessary only to have (1) a correct balance, (2) a pure specimen of substance to use as a weight, (3) an accurate burette filled with the appropriate solution. It is not necessary that the strength of this should be known; but the state of concentration should be such as to permit the necessary reaction to occur under the most favourable circumstances.

If a perfectly pure specimen of substance, say, calcium carbonate, be put into one scale of the balance, and be counterpoised with an impure specimen of the same substance, and both titrated with the same acid, and the number of c.c. used for the pure substance be called 100, the number of c.c. used for the impure substance will correspond to the percentage of pure calcium carbonate in the specimen examined.

The application of the process is, of course, limited to the use of such substances as are to be had pure, and whose weight is not variable by exposure; but where even a pure substance of one kind cannot be had as a weight, one of another kind may be used as a substitute, and the required result obtained by calculation. For instance, it is required to ascertain the purity of a specimen of sodium carbonate, and only pure calcium carbonate is at hand to use as a weight; equal weights of the two are taken, and the impure specimen titrated with acid. To arrive at the required result, it is necessary to find a coefficient or factor by which to convert the number of c.c. required by the sodium carbonate weighed on the calcium, into that which should be required if weighed on the sodium basis. A consideration of the relative molecular weights of the two bodies will give the factor thus—

$$\frac{\text{Calcium carbonate } 100{\cdot}07}{\text{Sodium carbonate } 106} = 0{\cdot}94406.$$

If, therefore, the c.c. used are multiplied by this number, the percentage of pure sodium carbonate will be obtained. On this principle, and with the exercise of a little ingenuity, the analysis of a number of substances may be carried out.

L. de Koningh has communicated to me a similar method devised by himself and Peacock, in which the same end is attained without the aid of a pure substance as standard, thus: say, a specimen of impure common salt is to be examined. A moderate portion is put on the balance and counterpoised with silver nitrate; the latter is then dissolved in water, made up to 100 c.c. and placed in a burette. The salt is dissolved in water, a few drops of potassium chromate added and titrated with the silver solution, of which 10 c.c. are required; the salt is therefore equal to 10 per cent. of its weight of silver nitrate, then—

$$16{\cdot}99 : 58{\cdot}46 : : 10 = 3{\cdot}44\ \%\ NaCl$$

Or, in the case of an impure soda ash, an equal weight of oxalic acid ($H_2C_2O_4, 2H_2O = 126{\cdot}048$) is taken and made up to 100 c.c.; the soda requires, say, 50 c.c. for saturation, or 50 per cent., then—

$$126{\cdot}048 : 106 : : 50 = 42{\cdot}04\ \%\ Na_2CO_3$$

It may happen that, in some cases, more than one portion of the reagent is required to decompose the substance titrated, and to provide against this two or more lots should be weighed in the first instance.

VOLUMETRIC ANALYSIS WITHOUT BURETTES OR OTHER GRADUATED INSTRUMENTS.

THIS operation consists in weighing the standard solutions on the balance instead of measuring them. The influence of variation in temperature is, of course, here of no consequence. The chief requisite is a delicate flask, fitted with a tube and blowing ball, or an instrument known as Schuster's alkalimeter may be used. A special burette has been devised for this purpose by Casamajor.[1] The method is capable of very accurate results, if care be taken in preparing the standard solutions and avoiding any loss in pouring the liquid from the vessel in which it is weighed. It occupies much more time than the usual processes of volumetric analysis, but at great extremes of temperature it is far more accurate.

---

[1] *C.N* 38, 98.

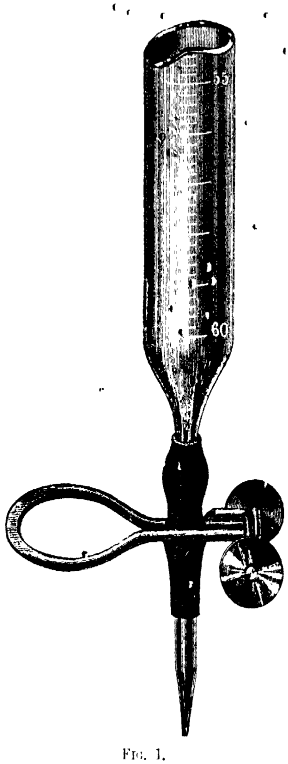

Fig. 1.

THE BURETTE.

THIS instrument is used for the delivery of an accurately measured volume of a standard solution. It invariably consists of a cylindrical glass tube of uniform bore graduated in cubic centimetres and with subdivisions in fifths or tenths. Usual capacities are 10, 25, and 50 c.c. graduated in $\frac{1}{10}$ c.c. and 100 c.c. graduated in $\frac{1}{5}$ c.c.

Numerous forms of burette have been invented and used in the past (e.g., Gay Lussac's, Geissler's, and Bink's),[1] but practically the only kinds in use at the present day are the following:—

Mohr's Burette.[2]—This is shown in its original form in fig. 1. The standard solution is delivered at will by pressing the pinch-cock, which clips a short piece of india-rubber tubing carrying a glass jet. The rubber tubing should be wired on to the burette tube by a short length of fine brass or copper wire, and the clip so adjusted that no drops of the solution can escape except when it is pressed. The form of this burette most frequently used, however, is made with a glass stop-cock, as in fig. 2, or fig. 3, a modification designed to prevent the tap from slipping out of place. Glass stop-cocks should be occasionally wiped dry and then smeared with a small quantity of vaseline as lubricant. A thin ring of rubber tubing (cut from burette tubing) stretched over the projecting narrow end of a glass tap is useful for keeping it in position. Burettes with glass stop-cocks have the advantage that they leave both hands of the operator disengaged and can be set to deliver drops at any desired rate. This kind must always be used for standard solutions of potassium permanganate and iodine, since both of these act upon rubber. Owing to the action of caustic alkalis on glass, tap burettes should not be employed for strong solutions of caustic potash or soda, unless emptied and washed immediately after use.

---

[1] For descriptions of these burettes see previous editions of this book.

[2] Karl Friedrich Mohr (1806-1879), German pharmacist, recognized as the leading scientific pharmacist of his time in Germany. He was the author of many improvements in analytical processes, and his methods of volumetric analysis were expounded in his *Lehrbuch der chemisch-analytischen Titrirmethode* (1855), which won the special commendation of Liebig and has run through many editions.

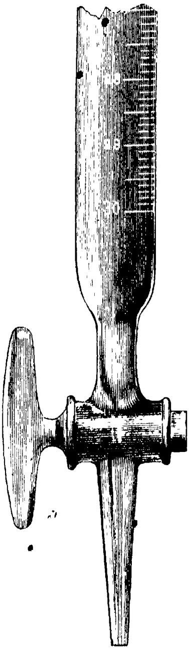

FIG. 2.

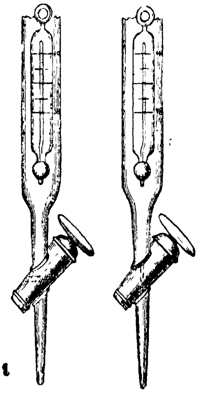

FIG. 3.

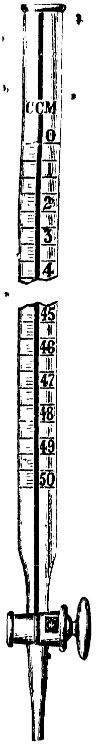

FIG. 4.

An addition to the burette, due to Schellbach, consists of a white enamelled band, with central blue ribbon, fused vertically at the back of the tube (*fig.* 4). This not only renders the graduation marks and figures more distinct, but enables the level of the liquid to be read with great ease and accuracy, as owing to refraction it appears pointed.

Schellbach's burette, however, has not proved altogether satisfactory in practice, and is admitted only to Class B tests at the National Physical laboratory. No enamel-back burettes are admitted to Class A tests. **Geissler's** burette is fitted with a glass stopper at the top having a small aperture in the side which can be brought opposite an opening in the burette tube when the instrument is in use. It is suitable for volatile solutions, and for general use.

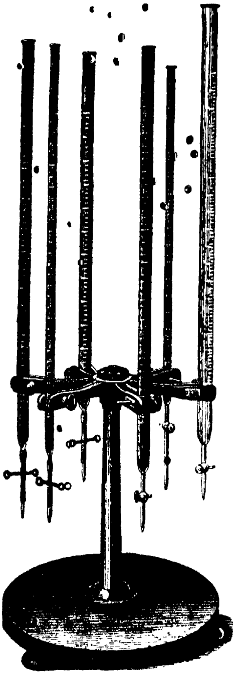

FIG. 5.

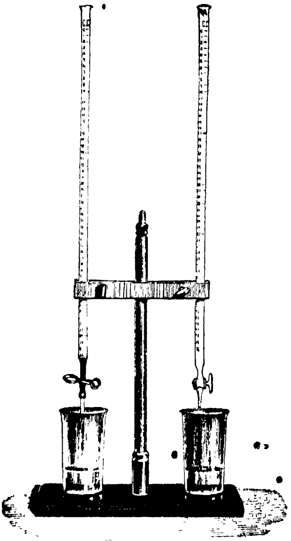

FIG. 6.

To facilitate filling, burettes are sometimes made with funnel-shaped tops.

When not in use, burettes should be covered with a short inverted test-tube to keep out the dust or inverted in the burette-stand jet uppermost: for those with funnel-shaped tops a greased glass plate may be used. The clips should also be removed from the rubber-tubing and hung up on the burette stand.

Two forms of burette stands, holding six and two burettes respectively are shown in figs. 5 and 6.

Mode of using a Mohr's Burette.—If the burette is empty, about 10 c.c. of the standard solution to be used should be poured into it through a small, short-stemmed funnel, run completely out into a dry vessel, and the same liquid passed through the burette again, drained completely out and thrown away. The burette is then nearly filled with the solution and a considerable amount of the liquid allowed to flow back into the bottle from which it is being filled. It is then filled up to a little above the zero mark and carefully adjusted to this point. This procedure is necessary in order to get completely rid of air bubbles, which often remain persistently in the rubber tubing until a current of liquid is run rapidly through it. Failure to get rid of these may easily cause the spoiling of a determination, as, if not removed, they generally make their unwelcome appearance during the process of titration. With glass stop-cocks, of course, air bubbles are readily seen.

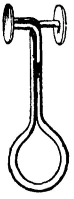
FIG. 7.

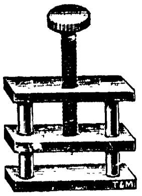

FIG. 8.

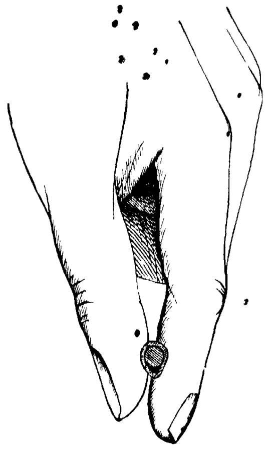
FIG. 9.

In place of the usual metal pinch-cock of a Mohr's burette shown in fig. 1 (also fig. 7) or Hofmann's clamp (fig. 8), a short piece of glass rod, which should not fit too tightly, may be inserted into the rubber tubing. By firmly squeezing the rubber surrounding the rod between the thumb and finger a narrow channel is opened, through which the liquid escapes, the rate of outflow being entirely controlled by the operator (see fig. 9).

When a certain standard solution is in constant requisition, it is convenient to have the burette in permanent communication with a reservoir from which it is filled as required. This is effected by means of a T piece of glass tubing (see fig. 10), inserted between the lower end of the burette and the clip and communicating by means of a length of rubber tubing and a second clip with a reservoir of a standard solution placed on a shelf above (fig. 12). On opening the latter clip the standard solution at once flows in without the formation of any bubbles, and further titrations can be immediately proceeded with. A neater arrangement than the above is the two-way glass stop-cock of Friedrich (see fig. 11).

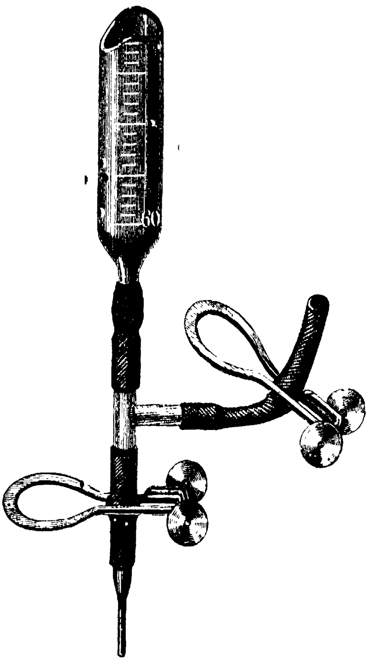

Fig. 10

The Titration of Hot Solutions.—For titrating hot or boiling solutions (e.g. in the determination of sugar by Fehling's solution) the ordinary Mohr's burette is not available, owing to the heating effect of the steam or vapour on the volume of the standard solution in the burette. In such cases a burette with long side-tube provided with a glass tap is used (Fig. 13); or a Mohr's burette with an extra long piece of rubber tubing, so that the burette stands at the side of the vessel that is being heated, and the rubber tube is brought over its edge, the clip being fixed midway. No heat will then reach the bulk of the standard solution in the burette, since there can be no conduction of heat past the clip.

Standardized Burettes.—Burettes that have been standardized at the National Physical Laboratory are supplied by most dealers in chemical apparatus. The tolerances or permissible errors for burettes are tabulated on p. 21.

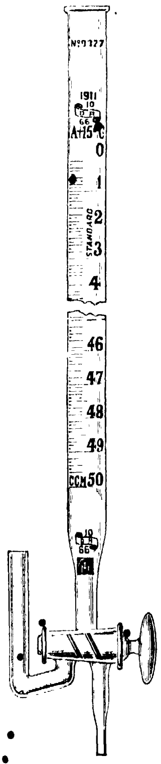

FIG. 11.

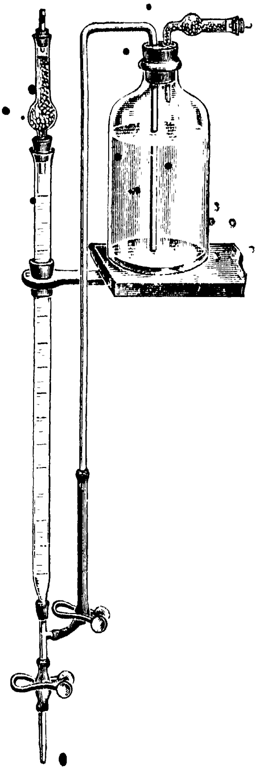

FIG. 12.

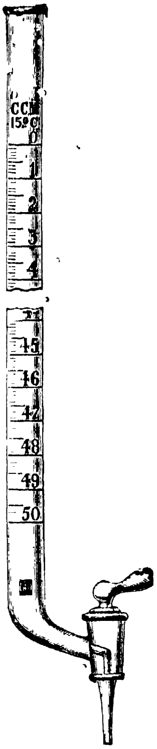

FIG. 13.

THE CORRECT METHOD OF READING BURETTES AND THE USE OF FLOATS.

In consequence of capillarity the surface of liquids in narrow tubes is always curved. Where the liquid wets the tube, its surface takes the form of a meniscus which is concave, as shown in fig. 14. In reading the heights of such liquids in tubes, the point where a graduation mark coincides with the bottom of the curve is taken.

Care must be taken that the eye is as nearly as possible on the same level as the meniscus, otherwise, owing to parallax, the reading may be too high or too low.

The eye may be assisted materially in reading the divisions on a graduated tube by using a piece of white paper or opal glass held at an angle of 30° or 40° from the burette and near the surface of the liquid, or a small card, the lower half of which is blackened, the upper remaining white. If the line of division between the black and white be held about an eighth of an inch below the surface of the liquid, and the eye brought on a level with it, the meniscus can then be seen by transmitted light, bounded below by a sharply defined black line. A card of this kind, sliding up and down a support, is of great use in verifying the graduation of burettes or pipettes with a cathetometer. Another good method is to use a piece of mirror, upon which are gummed two strips of black paper, half an inch apart; apply it in contact with the burette so that the eye can be reflected in the open space.

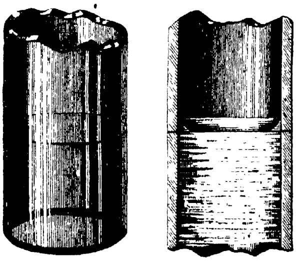

Fig 14.

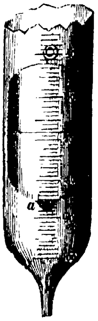

Fig. 15.

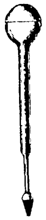

Fig. 16.

Burette Floats.—These are little accessories designed to enable the operator to obtain the most accurate reading of the burette. Erdmann's float was the first produced and is shown in fig. 15 and fig. 3. It consists of a small glass cylinder marked with a central transverse line and weighted with mercury. The reading is taken at the point where the line on the float coincides with a graduation mark of the burette. If not perfectly weighted this float tends to assume an oblique position in the liquid and is likewise apt to stick to the inner wall of the burette. Beutell's[1] float (fig. 16) gives good results if properly weighted so as to swim vertically in the liquid. A disadvantage is that it sticks to the side of the burette when this is emptied, hence it must be taken out every time the burette is to be refilled, and cleaned before being replaced. Rey's float, which is, perhaps, the best, has two bulbs, one of which projects above the surface of the liquid and carries the mark by which the reading is made. A float of some kind is almost indispensable for use with such dark-coloured solutions as decinormal iodine and permanganate. In all cases, of course, after the burette has been filled with the standard solution, this is run out until the mark on the float coincides with the zero graduation mark, then the titration is proceeded with and the final reading of the burette made in the same way.

---

[1] A. Beutell, *Z. f. angew. C.*, 1889, 2, 8.

How to Clean a Burette.—New burettes should always be cleaned before being used, and those in use should be cleaned occasionally. The most important thing to remove from a burette or pipette is grease. Ordinarily the simplest and best method of procedure is to pour a strong and hot solution of soap powder (i.e. soap and sodium carbonate) into the burette, closed at the lower end with a finger of the left hand, close the top with the right thumb and shake vigorously. As burettes are usually too narrow to allow of the introduction of a brush, some small pieces of filter paper and a little silver sand may advantageously be put into the tube before shaking. In some cases—e.g., a burette that has been used for barium hydroxide—stains may be removed by filling up with warm dilute hydrochloric acid and allowing to stand for a short time. Frequently simply shaking with water, filter paper and a little sand, does all that is required. In all cases the burette should finally be well washed with tap water, the outside wiped dry, fixed in a stand, rinsed out thoroughly with distilled water, covered with a test tube, and drained for several hours before being used. Dirty burettes are shown by the adherence of drops to the dirty parts.

Lubricant for Glass Stop-cocks.—Pure rubber 25, vaseline 20, hard paraffin 1 to 5. Melt the vaseline and paraffin and add the rubber in small pieces. Stir until a homogeneous mass results, avoiding overheating. A mixture of three parts of vaseline and one part of rubber similarly made also answers well.

THE PIPETTE.

THE pipettes used in volumetric analysis are of two kinds: (1) ordinary pipettes, which have but one mark and deliver a fixed quantity marked on the measure; (2) graduated pipettes, the stems of which are graduated to deliver various quantities at the discretion of the analyst. In using the former, they are first filled from the jet to about 1 cm. above the mark, then allowed to run down just to the mark. Any drops adhering to the jet are removed. The liquid is then allowed to run out into the vessel where it is required, the point of the jet touching the wall of the vessel. After the continuous outflow has ceased, the pipette is allowed to drain for 15 seconds and the jet is then stroked off the wall of the vessel. The standard temperature is 15° C.

In the larger pipettes, the upper end is narrowed to about ⅛ inch, so that the pressure of the finger is sufficient to arrest the flow at any point.

Pipettes are invariably filled by sucking the upper end with the mouth, unless the liquid is volatile or highly poisonous, in which case it is best to use some other kind of measurement. Beginners invariably find a difficulty in quickly filling the pipette above the mark, and stopping the fluid at the exact point. Practice with pure water is the only method of overcoming this.

Fig. 17 shows an ordinary pipette and also a graduated pipette of medium size. It must be borne in mind that the pipette graduated throughout the stem is not a reliable instrument for accurate titration, owing to the difficulty of stopping the flow of liquid at any given point and reading off the exact measurement. Its chief use is in the approximate determination of the strength of any standard solution in the course of preparation.

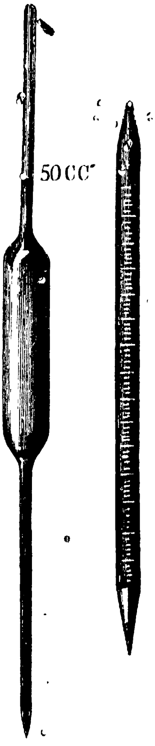

FIG. 17.

Fig 18 shows a very useful form of pipette for measuring strong acids or alkalis, etc., the bulb preventing the entrance of any liquid into the mouth.

For permissible errors in pipettes, see p. 20.

THE MEASURING FLASK.

MEASURING flasks (fig. 19) serve to make up standard solutions to a given volume, and also enable the analyst, with the aid of pipettes, to obtain aliquot portions of a substance to be tested. They should be as narrow in the neck as is compatible with easy filling and emptying, and the mark should be situated below the middle of the neck, so as to allow room for thoroughly mixing the contents by shaking.

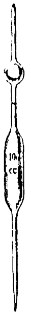

FIG. 18.

Measuring flasks are made either to *contain* or to *deliver* the quantities marked on them, and the temperature at which they have been standardized should invariably be marked on also. Ordinary flasks with one mark are always taken to *contain* the amount specified. Vessels standardized at the National Physical Laboratory, Teddington, are marked with the letter D when they are meant to deliver; if meant for both content and delivery the letter D is placed above the upper, and the letter C below the lower, mark. The standard temperature is 15° C. Thus, a standardized flask marked "1 litre 15° C." is such that, at a temperature of 15° C., the volume of the contents of the flask is the same as that of a kilogram of water at a temperature of 4° C. Since, however, the density of water at 15° C. is 0·99913 gm. per c.c. the weight of water at 15° C. which fills the flask up to the mark is 999·13 gm., not 1000 gm.

Measuring flasks are ordinarily made of 50, 70, 100, 200, 250, 500, 1000 and 2000 c.c. capacity. Flasks for delivery should be gradually tilted till nearly vertical, drained for half a minute, and the last drop removed by touching the side of the vessel into which they are being emptied.

For permissible errors in graduated flasks, see p. 19.

W. B. Giles has described a modified flask,[1] shown in fig. 20. It is handy in making up standard solutions where the reagent cannot be weighed in an absolutely pure state, for instance, sulphuric acid, ammonium thiocyanate, or uranic salts. Such a quantity, however, is taken as will give a solution about a ninth or tenth too strong, and the measure is made up to 1100 c.c. The real strength is then taken by two titrations on 25 or 30 c.c. with a known standard, so that its exact working strength is known; the remainder of the 100 c.c. is then removed down to the 1000 c.c. mark, and a slight calculation will show how much water has to be added to the 1000 c.c. to make a correct solution. If only a litre is made up, an unknown volume is left in the flask, and it must be transferred to a measuring cylinder, where, owing to the large diameter of the vessel, the graduation can never be so accurate as in the narrow neck of the flask. Should the solution prove to be only about a tenth too strong, the necessary dilution may be made in the flask itself; but if stronger than this, the flask must be emptied into the store bottle and rinsed out with the measured quantity of water required, which is then drained into the store bottle, and the whole carefully mixed.

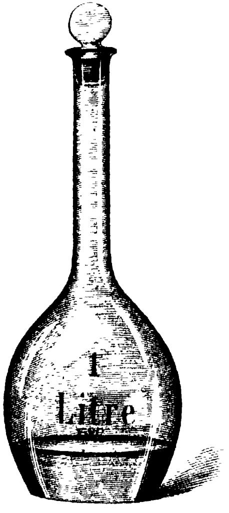

Fig. 19.

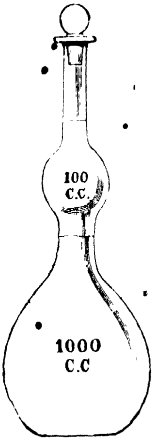

Fig. 20.

In addition to the measuring flasks it is necessary to have graduated vessels of cylindrical form for the purpose of preparing standard solutions, etc.

---

[1] *C. N.* 69, 99.

In the verification of a flask, the vessel is first carefully cleaned, and filled with distilled water to a few mm. above the mark, care being taken to avoid wetting the neck above the level. The surface is then adjusted to the mark by removing small quantities of water with a fine capillary tube. Flasks intended for "delivery" are emptied into a glass by gradually inclining them, until, when the continuous stream of the liquid has ceased, they are nearly vertical. In this position they are allowed to drain for half a minute, and the lip is then stroked against the glass.

Pipettes.—The delivery tip must conform with the conditions given for burette jets (2)—see p. 21. The outlet must be of such a size that the outflow of water occupies the time given in the table below:—

Capacity c.c.	5	10	50	100	250	500
Time of outflow—secs.	10-20	15-30	20-40	30-60	45-90	60-120

NOTE.—For capacities not tabulated the delivery times are those of the next larger tabulated capacity.

The tolerances allowed on pipettes, whether ordinary or automatic, are:—

Capacity c.c.	2	5	10	20	30	50	100	150	250
Tolerance ± c.c. for content or delivery	0·006	0·01	0·015	0·02	0·025	0·035	0·05	0·07	0·08

NOTE.—For capacities not tabulated the tolerances are those given for the next larger tabulated capacity.

The time of outflow and the drainage time (15 secs.) must be marked on all pipettes. For example, a suitable inscription for a 50 c.c. pipette would be—

50 c.c.
D. 15° C.
(30 + 15) secs.

The actual time of outflow must be within the limits given above, and also must not differ from the time etched on the pipette by more than the amounts tabulated below:—

Marked time of outflow—secs.	30	60	90	120
Maximum difference allowed between marked and actual time of outflow ± secs.	2	4	6	8

Ordinary pipettes are clamped vertically for test, and filled with water to a short distance above the mark. Water is run out until the meniscus is on the mark and the outflow is then stopped. The drop adhering to the tip is removed by bringing the surface of some water contained in a beaker into contact with the tip and then removing it without jerking

The pipette is then allowed to deliver into a clean weighed vessel held slightly inclined so that the tip of the pipette is in contact with the side of the vessel. The pipette is allowed to drain for a quarter of a minute after outflow has ceased, the tip still being in contact with the side of the vessel. At the end of the draining time the receiving vessel is removed from contact with the tip of the pipette, thus removing any drop adhering to the outside of the pipette. To determine the instant at which the outflow ceases, the motion of the water surface down the delivery tube of the pipette is observed, and the delivery time is considered to be complete when the meniscus comes to rest slightly above the end of the delivery tube. The quarter of a minute draining time is counted from this moment.

Burettes and Graduated Pipettes.—(1) Enamel-back burettes are not admitted to Class A tests. Burettes without taps are also excluded. Both, however, are admitted to Class B tests. The graduated portion of graduated pipettes must not exceed 35 cm. in length.

(2) The jets must be made with a gradual taper. A sudden constriction at the orifice is not allowed. The end of the jet must be ground off true, and the ground surface must be smooth.

(3) The diameter of the outlet must be of such a size that the time occupied by the outflow of water from the zero mark to the lowest graduation mark, the stop-cock being fully open, conforms with the limits given below :—

Length graduated cm.	15	20	25	30	35	40	45	50	55	60	65	70	75
Time of outflow—secs.	30 to 60	40 to 80	50 to 100	60 to 120	70 to 140	80 to 160	90 to 180	100 to 200	110 to 220	120 to 240	130 to 260	140 to 280	150 to 300

NOTE.—For lengths not tabulated the times allowed are those corresponding to the next larger tabulated length.

The tolerances allowed on burettes and graduated pipettes are as follows :—

Total capacity c.c.	2	10	30	50	75	100	200
Maximum error allowed at any point and also maximum difference allowed between the errors at any two points for content or delivery ± c.c.	0·01	0·02	0·03	0·04	0·06	0·08	0·15

NOTE.—(*a*) For capacities not tabulated, the tolerances are the same as those given for the next larger tabulated capacity. (*b*) The tolerances apply to the whole of the graduated portion and to any fraction of it. Thus, for example, a 50 c.c. burette may be in error by ± 0·04 c.c. at any point provided that the difference between the errors at any two points tested does not exceed 0·04 c.c.

Burettes and graduated pipettes are clamped vertically for test, and filled with water to a short distance above the zero mark. Water is then slowly run out until the meniscus is exactly on the zero mark.

The drop adhering to the tip is then removed by bringing the tip into contact with the inside of a glass beaker. The instrument is then allowed to deliver freely, i.e., in the case of burettes, with the stop-cock fully open, into a clean weighed vessel. It is necessary, however, to arrest the full flow of liquid in time to obtain control over the final movement of the water surface and to bring the meniscus to rest accurately on the line to be tested. The instrument is, therefore, allowed to deliver freely until the water surface is approximately 1 cm. from the line to be tested. The rate of outflow is then reduced and the motion of the water surface brought under control so that an accurate setting can be made on the line in question. No period of waiting for drainage is allowed. The drop adhering to the tip after the setting has been made is removed by bringing the side of the receiving vessel into contact with the tip.

Graduated Cylinders.—(1) Graduated cylinders calibrated for "delivery" are not admitted to Class A tests.

(2) Tolerances.

Total capacity c.c.	5	10	25	50	100	250	500	1000	2000
Maximum error allowed at any point, and also maximum difference allowed between the errors at any two points for content ± c.c.	0·04	0·06	0·10	0·15	0·25	0·50	1·0	1·5	2·5

The notes (*a*) and (*b*) relating to tolerances on burettes apply also to graduated cylinders.

An interesting Report on the Standardization of Laboratory Glassware is given in the *J.S.C.I.*, 1919, **38**, 280 R. Special attention is drawn to the errors that may arise through the use of quick delivery burettes.

Cylinders.—The only method of calibrating these vessels is to measure into them repeatedly various volumes of water from delivery pipettes of proved accuracy, taking precautions as to level, meniscus, and the proper drainage of the pipette after each delivery.[1]

Preservation of Solutions.—There are test solutions which, in consequence of their proneness to decomposition, cannot be kept at any particular strength for a length of time; consequently they must be titrated on every occasion before being used. Stannous chloride and sulphurous acid are examples of such solutions. Special vessels have been devised for keeping solutions liable to alter in strength by access of air, as shown in figs. 22 and 23.

Fig. 22 is especially applicable to caustic alkali solutions, the tube passing through the rubber stopper being filled with dry soda-lime, resting on cotton wool.

---

[1] An excellent method of calibration for volumetric instruments is given by Morse and Blalock (*Amer. Chem. Journ.* **16**, 479).

Fig. 23, designed by Mohr, is a considerable improvement upon this, since it allows of the burette being filled with the solution from the store bottle quietly, and without any access of air whatever. The vessel can be used for caustic alkalis, baryta, stannous chloride, permanganate, and sulphurous acid, or any other liquid liable to undergo change by absorbing oxygen. Rubber stoppers should be used for these bottles; and a thin layer of white mineral oil is poured on the top of the solution, where, owing to its low density, it always floats, placing an impermeable division between the air and the solution; and as this oil is not affected by these solutions in their diluted state, this form is of great advantage. Fig. 23 can be improved by having a two-holed rubber stopper—one hole is used for a tapped funnel, through which the bottle is filled, the other hole contains a small tapped tube, which is opened when drawing the solution out or when filling the bottle. For a still better arrangement see fig. 12. Solutions not affected chemically by contact with air should be kept in bottles, the corks or stoppers of which keep them perfectly closed, and tied over with india-rubber or bladder to prevent evaporation,

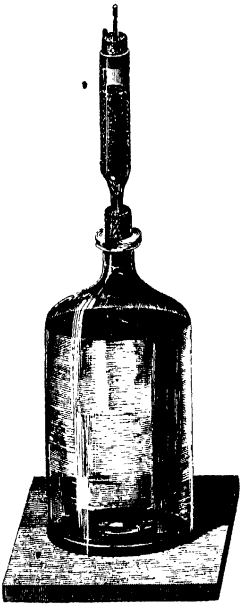

FIG. 22.

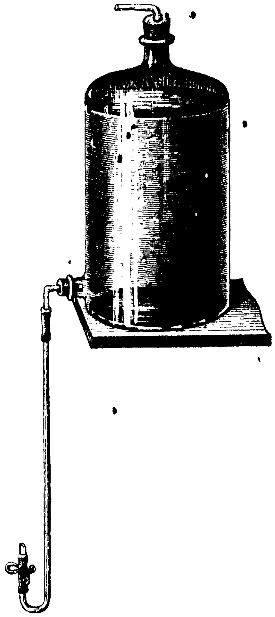

FIG. 23.

and should further be always shaken before use, when they are not quite full. The influence of bright light upon some solutions is very detrimental to their chemical stability; hence it is advisable to preserve some solutions not in immediate use in the dark, and at a temperature not exceeding 15° or 16° C.

The apparatus devised by J. C. Chorley, and shown in fig. 24, will be found useful for preserving and delivering known volumes of such solutions as alcoholic potash, which are liable to alteration by exposure to air. The wash bottle inserted in the cork of the large store bottle contains a solution of caustic soda, and serves to wash all air entering the large bottle. By means of the three-way stop-cock at the bottom of the apparatus the solution is allowed to fill the pipette and overflow into its upper chamber, the excess being caught in the small side bulb and reservoir; this solution serves to wash all air entering the pipette when the stop-cock is turned to deliver the solution, which is run off to a mark just above the tap. When full, the side reservoir may be emptied by withdrawing the small ground stopper.

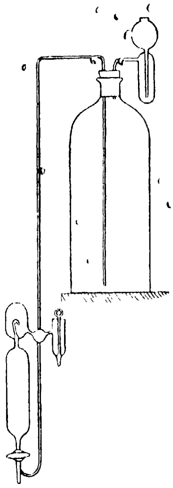

Fig. 24.

J. H. Coste[1] has pointed out that a layer of oil is useless for preventing the transmission of the gases of the air. He found that the absorption of oxygen from air by water under relatively thick layers of various oils was considerable. Gniewosz and Walfisez found that "the coefficient for the absorption of oxygen and many other gases by petroleum is much higher than that for water. The authors consider it illusory, therefore, to try to protect liquids from oxidation by covering them with a layer of petroleum."

ON THE SYSTEM OF WEIGHTS AND MEASURES TO BE ADOPTED IN VOLUMETRIC ANALYSIS.

It is much to be regretted that the metric system of weights and measures used on the Continent is not universally adopted, for both scientific and general purposes, throughout the civilized world. The two great advantages of the metric system are that it is, first, a decimal system and, secondly, a simply-related system. A short description of the origin and development of this system may not here be out of place.

The Metric System is founded on the *metre*, which was originally intended to be one ten-millionth part of a quadrant of the meridian through Paris, in other words, one forty-millionth part of the circumference of the earth. Subsequent measurements, however, have shown that the metre does not exactly represent this; hence the unit becomes an arbitrary measure after all.

---

[1] *J.S.C.I.*, 1917, **36**, 954.

All the multiples of units in the Metric System are indicated by Greek prefixes, all fractions or submultiples by Latin prefixes, thus :—

kilo = a thousand times
hecto = a hundred times
deca = ten times
the unit to which it is prefixed.

milli = a thousandth part, or ·001
centi = a hundredth part, or ·01
deci = a tenth part or ·1
of the unit to which it is prefixed.

For example, a hectogram = 100 grams
a millimetre = one-thousandth part of a metre, or ·001 metre.

The decimals of a metre are abbreviated thus :—

Millimetres = mm.
Centimetres = cm.
Decimetres = dm.

The unit of surface is the *are*, which is a square whose side is 10 metres. Consequently it equals 100 square metres and is indicated thus : 1 are = 100 m^2.

Vessels used in volumetric analysis are generally graduated in cubic centimetres, the cubic centimetre being the volume occupied by a cube, each of whose sides is one centimetre in length.

Volumes are also measured in terms of the litre, which is defined as the volume occupied by one kilogram of pure water at its maximum density (about 4° C.) and under standard pressure (760 mm.). The weighing is corrected for the buoyancy of the air. The subdivisions of the litre are the decilitre, centilitre, and millilitre.

Originally it was intended that a kilogram should be the mass of 1000 c.c. of water at the temperature of its maximum density, and accordingly the litre would have been 1000 c.c. in volume.

The most recent determinations have shown that this is not the case and that

1 litre = 1000·027 cubic centimetres (c.c., c.cm., or cm.^{3})

There is, therefore, a very slight difference between the cubic centimetre and the millilitre, or thousandth part of a litre, a difference so slight that for nearly all purposes it is negligible.

F. Mohr introduced in 1855 a system of graduation the unit of which is the volume occupied by a quantity of pure water which, when weighed in air against brass weights, at a stated standard temperature (usually 15° C.), has an apparent weight of one gram. Vessels graduated on this system should bear the word "Gramme" or the letters "Grm." For a standard temperature of 15° C., the volume corresponding with 1000 "Grm." = 1001·980 c.c.

Obviously, then, volumetric apparatus graduated in cubic centimetres cannot be used interchangeably with that graduated on Mohr's system. Either one system or the other must be rigidly adhered to.

The National Physical Laboratory strongly recommends that cubic centimetres should be used to the exclusion of both Mohr's grammes and grains.

The usual standard temperature for volumetric vessels is 15° C., which means that a vessel contains its nominal content of water when the vessel is at 15° C. This is usually judged by the water being steady at 15° C., and for exactness the surrounding air should be at 15° C. also. When the vessel is at a different temperature, its volume alters in accordance with the coefficient of cubical expansion of the glass. Various other temperatures in addition to the standard 15° C. are, however, in common use, as for instance, 20° C. for vessels employed in connection with polarimeters or viscosimeters, 80° or 82° F. for vessels intended for tropical climates and so on.

The British equivalents of the principal metric units are as follows :—

1 metre = 39·370113 inches.
1 are = 119·60 square yards.
1 litre = 1·75980 pints.
" = 0·2200 gallon.
1 kilogram = 2·2046223 lb.
1 gram = 15·43236 grains.

Variations of Temperature.—In the preparation of standard solutions one thing must especially be borne in mind, namely, that saline substances on being dissolved in water have a considerable effect upon the volume of the resulting liquid. The same is also the case in mixing solutions of various salts or acids with each other.[1]

In the preparation of strong solutions the contraction in volume is as a rule considerable. Hence, in preparing such solutions for volumetric analysis, or in diluting such solutions to a given volume for the purpose of removing aliquot portions subsequently for examination, sufficient time must be given for liquids to acquire their constant volume at the standard temperature. If the strength of a standard solution is known for one temperature, the strength corresponding to another temperature can only be calculated if the rate of expansion by heat of the liquid is known. The variation cannot be estimated by the known rule of expansion of distilled water; for Gerlach has shown that even weak solutions of acids and salts expand far more than water for certain increments of temperature. The rate of expansion for pure water is known, and may be used for the purpose of verifying the graduation of instruments where extreme accuracy is required. The following table furnishes the data for correction.

The table on opposite page was given in the Report of the International Conference on the Unification of Methods of Analysis of Alimentary Substances; Paris, 1910.

G is the quantity to be subtracted from 1000 to obtain the weight of 1000 c.c. of water at the temperature given. Thus at 20° and 760 mm. 2·82 must be deducted from 1000 = 997·18.

Bearing the foregoing remarks in mind, therefore, the safest plan in the operations of volumetric analysis, so far as measurement is concerned, is to use solutions as dilute as possible. Absolute accuracy in determining the strength of standard solutions can be secured only by the process of weighing, the ratio of the weight of the solution to the weight of active substance in it being independent of temperature.

---

[1] See Gerlach, "Specifische Gewichte der Salzlosungen"; also Gerlach, "Sp. Gewichte von wasserigen Losungen," *Z. a. C.*, **8**, 245.

TABLE.—SHOWING THE NUMBER OF GRAMS (G) THAT MUST BE SUBTRACTED FROM 1 KILOGRAM TO OBTAIN THE WEIGHT OF 1 LITRE OF DISTILLED WATER AT VARIOUS TEMPERATURES AND PRESSURES, WHEN WEIGHED IN AIR WITH WEIGHTS OF A DENSITY OF 8·5.

Temperature.	70 cm.	71 cm.	72 cm.	73 cm.	74 cm.	75 cm.	76 cm.	77 cm.	78 cm.	79 cm	80 cm.
C.	G.	G.	G.	G.	G.	G.	G.	G.	G.	G.	G.
10° . .	1·29	1·30	1·31	1·33	1·34	1·36	1·37	1·38	1·40	1·41	1·42
11° . .	1·38	1·39	1·41	1·42	1·43	1·45	1·46	1·47	1·49	1·50	1·52
12° . .	1·48	1·50	1·51	1·52	1·54	1·55	1·57	1·58	1·59	1·61	1·62
13° . .	1·60	1·61	1·63	1·64	1·65	1·67	1·68	1·70	1·71	1·72	1·74
14° . .	1·73	1·74	1·76	1·77	1·78	1·80	1·81	1·82	1·84	1·85	1·86
15° . .	1·87	1·88	1·90	1·91	1·92	1·94	1·95	1·96	1·98	1·99	2·01
16° . .	2·02	2·04	2·05	2·06	2·07	2·09	2·10	2·12	2·13	2·14	2·16
17° . .	2·19	2·20	2·21	2·23	2·24	2·25	2·27	2·28	2·29	2·31	2·32
18° . .	2·36	2·38	2·39	2·40	2·42	2·43	2·44	2·46	2·47	2·48	2·50
19° . .	2·55	2·56	2·57	2·59	2·60	2·61	2·63	2·64	2·65	2·67	2·68
20° . .	2·74	2·76	2·77	2·78	2·80	2·81	2·82	2·84	2·85	2·86	2·88
21° . .	2·95	2·97	2·98	2·99	3·00	3·02	3·03	3·04	3·06	3·07	3·08
22° . .	3·17	3·18	3·20	3·21	3·22	3·24	3·25	3·26	3·28	3·29	3·30
23° . .	3·40	3·41	3·43	3·44	3·45	3·46	3·48	3·49	3·50	3·52	3·53
24° .	3·63	3·65	3·66	3·67	3·69	3·70	3·71	3·73	3·74	3·75	3·77
25° . .	3·88	3·90	3·91	3·92	3·94	3·95	3·96	3·98	3·99	4·00	4·01

Casamajor[1] has made use of the data given by Matthiessen in his researches on the expansion of glass, water, and mercury, to construct a table of corrections to be used when using any weak standard solution at a different temperature from that at which it was originally standardized.

The expansion of water is different at different temperatures; the expansion of glass is known to be constant for all temperatures up to 100° C. The correction of volume, therefore, in glass burettes must be the known expansion of each c.c. of water for every 1° C., less the known expansion of glass for the same temperature.

Casamajor's results are shortly given in the following table.

The normal temperature is 15° C.; and the figures given are the relative contractions below, and expansions above, 15° C. in c.c.

Deg. C.		Deg. C.	
7	− ·000612	24	+ ·001686
8	− ·000590	25	+ ·001919
9	− ·000550	26	+ ·002159
10	− ·000492	27	+ ·002405
11	− ·000420	28	+ ·002657
12	− ·000334	29	+ ·002913
13	·000236	30	+ ·003179
14	− ·000124	31	+ ·003453
15	Normal	32	+ ·003739
16	+ ·000147	33	+ ·004035
17	+ ·000305	34	+ ·004342
18	+ ·000473	35	+ ·004660
19	+ ·000652	36	+ ·004987
20	+ ·000841	37	+ ·005323
21	+ ·001039	38	+ ·005667
22	+ ·001246	39	+ ·006040
23	+ ·001462	40	+ ·006382

---

[1] C.N., 35, 160.

By means of these numbers it is easy to calculate the volume of liquid at 15° C. corresponding to any volume observed at any temperature. If 35 c.c. of solution has been used at 27° C., the table shows that 1 c.c. of water in passing from 15° to 27° is increased to 1·002405 c.c.; therefore, by dividing 35 c.c. by 1·002405 is obtained the quotient 34·915 c.c., which represents the volume at 15° corresponding to 35 c.c. at 27°. The operation can be simplified by obtaining the factor, thus:—

$$\frac{1}{1{\cdot}002405} = 0{\cdot}997586$$

and 35 × 0·9976 = 34·916.

A table can thus be easily constructed which would show the factor for each degree of temperature.

These corrections are useless for concentrated solutions, such as normal alkalis or acids; with great variations of temperature these solutions should be used by weight.

For the commoner normal solutions, however, Schlosser[1] has worked out the following table:—

TABLE FOR THE CORRECTION OF THE VOLUME OF WATER, NORMAL, AND DECI-NORMAL SOLUTIONS TO THE TEMPERATURE OF 15° C.

IN C.C. PER 1 LITRE OF

Temperature.	Water and N/10 Solutions	N/1 HCl	N/1 $H_2C_2O_4$	N/1 H_2SO_4	N/1 HNO_3	N/1 Na_2CO_3.	N/1 NaOH.
C.							
5° . .	+ 0·60	+ 1·26	+ 1·33	+ 1·94	+ 2·00	+ 2·03	+ 2·18
6° . .	0·60	1·18	1·25	1·79	1·84	1·87	1·99
7° . .	0·59	1·10	1·16	1·63	1·68	1·69	1·80
8° . .	0·56	1·00	1·05	1·46	1·50	1·50	1·60
9° . .	0·52	0·88	0·94	1·28	1·31	1·31	1·39
10° . .	0·46	0·76	0·81	1·09	1·11	1·11	1·18
11° . .	0·40	0·63	0·67	0·89	0·91	0·90	0·96
12° . .	0·33	0·48	0·52	0·68	0·69	0·69	0·73
13° . .	0·22	0·33	0·35	0·46	0·46	0·47	0·50
14° . .	+ 0·12	+ 0·17	+ 0·18	+ 0·23	+ 0·23	+ 0·24	+ 0·25
15° . .	0·00	0·00	0·00	0·00	0·00	0·00	0·00
16° . .	− 0·13	− 0·18	− 0·20	− 0·24	− 0·25	− 0·24	− 0·25
17° . .	0·27	0·36	0·40	0·49	0·50	0·49	0·51
18° . .	0·42	0·56	0·61	0·75	0·76	0·75	0·78
19° . .	0·59	0·76	0·82	1·02	1·03	1·02	1·05
20° . .	− 0·76	− 0·97	− 1·05	− 1·30	− 1·30	− 1·29	− 1·33
21° . .	0·95	1·19	1·29	1·58	1·58	1·57	1·62
22° . .	1·14	1·41	1·54	1·86	1·87	1·85	1·92
23° . .	1·35	1·64	1·80	2·15	2·17	2·14	2·23
24° . .	1·56	1·88	2·07	2·45	2·47	2·44	2·54
25° . .	1·79	2·14	2·34	2·76	2·78	2·75	2·85
26° . .	2·02	2·40	2·62	3·08	3·10	3·06	3·17
27° . .	2·27	2·67	2·90	3·41	3·43	3·38	3·50
28° . .	2·52	2·95	3·19	3·75	3·76	3·70	3·83
29° . .	2·75	3·23	3·49	4·09	4·10	4·04	4·17
30° . .	− 3·06	− 3·52	− 3·82	− 4·43	− 4·44	− 4·38	− 4·52

---

[1] *Ch. Z.*, 1904, 4; 1905, 510.

VOLUMETRIC ANALYSIS BASED ON THE SYSTEM OF CHEMICAL EQUIVALENCE AND THE PREPARATION OF NORMAL SOLUTIONS.

WHEN analysis by measure first came into use, the test solutions were generally prepared so that each substance to be tested had its own special reagent; and the strength of the standard solution was so calculated as to give the result in percentages. Consequently, in alkalimetry, a distinct standard acid was used for soda, another for potash, a third for ammonia, and so on, necessitating a great variety of standard solutions. Griffin and Ure appear to have been the first to suggest the use of standard test solutions based on the atomic system; and following in their steps Mohr has worked out and verified many methods of analysis which are of great value to all who concern themselves with scientific and especially with technical chemistry. Not only has Mohr done this, but he has enriched his processes with so many original investigations, and improved the necessary apparatus to such an extent, that he may with justice be called the father of the volumetric system.

Normal Solutions.—It is of great importance that no misconception should exist as to what is meant by a normal solution; but it does unfortunately occur.[1]

Normal solutions may be defined as follows:—

A normal solution of a reagent is one that contains in a litre that proportion of its molecular weight in grams which corresponds to 1·008 gram of available hydrogen or its equivalent.

As in every case where a normal solution is used, attention is directed to a particular reaction and the part played therein by the particular elements or ions involved, the definition may be expressed thus:—

A normal solution of a reagent is one that contains in a litre "a weight of the reagent equal to the quotient obtained by dividing the gram equivalent by the sum of the utilized valencies of the specially considered element or ion in the specified reaction" (F. A. Gooch).

Seminormal, pentinormal, decinormal and centinormal solutions are also required and are shortly designated as $^N/_2$ $^N/_5$ $^N/_{10}$ and $^N/_{100}$ solutions.

Thus, a normal solution of hydrochloric acid contains 36·468 gm. in a litre, because this weight of the acid contains 1·008 gm. of hydrogen; similarly normal sodium hydroxide contains 40·008 gm. per litre. Oxalic acid contains in the molecule two atoms of hydrogen, both available, and consequently normal oxalic acid contains $\frac{126\cdot048}{2}$ = 63·024 gm. of the crystallized acid ($H_2C_2O_4 2H_2O$) in the litre. Similarly, a normal solution of sodium phosphate would be made by dissolving one-third of the molecular weight of the crystallized salt, in grams, in water and diluting the solution to 1 litre, because orthophosphoric acid contains 3 atoms of available hydrogen in its molecule.

In preparing a normal solution of potassium permanganate for use as an oxidizing agent we know that $K_2Mn_2O_8$ gives up 5 atoms of available oxygen, equivalent to 10 atoms of available hydrogen. Hence, a normal solution of potassium permanganate contains $\frac{316\cdot06}{10}$ = 31·606 gm. of the crystallized salt per litre.

---

[1] See Allen, *C.N.*, **40**, 239, also *Analyst*, **13**, 181.

Normal alkali solutions are always such that a given volume requires for neutralization an equal volume of a normal acid solution.

Other instances will be given later on and explained in detail in their proper place.

A further illustration may be given in order to show the method of calculating the results of this kind of analysis.

Each c.c. of N/10 silver nitrate solution will contain $\frac{1}{10000}$ of the atomic weight of silver = 0·010788 gm., and will exactly precipitate $\frac{1}{10000}$ of the atomic weight of chlorine = 0·003546 gm. from any solution of a chloride.

In the case of normal oxalic acid each c.c. will contain $\frac{1}{2000}$ of the molecular weight of the crystallized acid = 0·063024 gm., and will neutralize $\frac{1}{2000}$ of the molecular weight of sodium carbonate = 0·053 gm., or will combine with $\frac{1}{2000}$ of the atomic weight of a dyad metal such as lead = 0·10356 gm., or will exactly saturate $\frac{1}{1000}$ of the molecular weight of sodium hydrate = 0·040 gm., and so on.

The great convenience of this equivalent system is that the numbers used as coefficients for calculation in any analysis are familiar, and the solutions agree with each other, volume for volume. We have, hitherto, however, looked only at one side of its advantages. For technical purposes the plan allows the use of all solutions of systematic strength, and simply varies the amount of substance tested according to its equivalent weight.

Thus, the normal solutions are—

Crystallized oxalic acid	= 63·024 gm.	per litre.
Sulphuric acid	= 49·038 gm.	,,
Hydrochloric acid	= 36·468 gm.	,,
Nitric acid	= 63·018 gm.	,,
Anhydrous sodium carbonate	= 53 gm.	,,
Sodium hydroxide	= 40·008 gm.	,,
Ammonia	= 17·034 gm.	,,

100 c.c. of any one of these normal acids should exactly neutralize 100 c.c. of any of the normal alkalis, or the corresponding amount of pure substance which the 100 c.c. contain. In commerce we continually meet with substances used in manufactures which are not pure, and it is necessary to know how much pure substance they contain.

Take, for instance, refined soda ash (sodium carbonate). If it were absolutely pure, 5·3 gm. of it should require exactly 100 c.c. of any normal acid to saturate it. If we therefore weigh that quantity, dissolve it in water, and deliver into the solution the normal acid from a burette, the number of c.c. required to saturate it will show the percentage of pure sodium carbonate in the sample. Suppose 90 c.c. are required = 90 per cent.

Again—a manufacturer buys common oil of vitriol, and requires to know the exact percentage of pure monohydrated acid in it; 4·9 gm. are weighed, diluted with water, and normal alkali delivered in from a burette till saturated; the number of c.c. used will be the percentage of real acid. Suppose 58·5 c.c. are required = 58·5 per cent.

Or, suppose the analyst desires to know the equivalent percentage of sodium oxide, free and combined, contained in the above sample of soda ash, without calculating it from the carbonate found as above, 3·1 gm. are treated as before, and the number of c.c. required is the percentage of sodium oxide. In the same sample 52·6 c.c. would be required = 52·6 per cent. of sodium oxide, or 90 per cent. of sodium carbonate.

Method for Percentage of Purity in Commercial Substances.—The rules, therefore, for obtaining the percentage of pure substances in any commercial article, such as alkalis, acids, and various salts, by means of systematic normal solutions such as have been described are these—

1. With normal solutions $\frac{1}{10}$ or $\frac{1}{20}$ (according to its atomicity) of the molecular weight in grams of the substance to be analysed is to be weighed for titration, and the number of c.c. required to produce the desired reaction is the percentage of the substance whose atomic weight has been used.

With decinormal solutions $\frac{1}{100}$ or $\frac{1}{200}$ of the molecular weight in grams is taken, and the number of c.c. required will, in like manner, give the percentage.

Factors, or Coefficients, for the Calculation of Analyses.—It frequently occurs that from the nature of the substance, or from its being in solution, this percentage method cannot be conveniently followed. For instance, suppose the operator has a solution containing an unknown quantity of caustic potash, the strength of which he desires to know; a weighed or measured quantity of it is brought under the normal acid burette and exactly saturated, 32 c.c. being required. The calculation is as follows:—

The molecular weight of potassium hydroxide being 56·11: 100 c.c. of normal acid will saturate 5·611 gm.; therefore, as 100 c.c. are to 5·611 gm., so are 32 c.c. to x, $\frac{5·611 \times 32}{100} = 1·796$ gm. KHO.

The simplest way, therefore, to proceed, is to multiply the number of c.c. of test solution required in any analysis by the $\frac{1}{1000}$ (or $\frac{2}{1000}$ if bivalent) of the molecular weight of the substance sought, which gives at once the amount of substance present.

An example may be given—1 gm. of marble or limestone is taken for the determination of pure calcium carbonate, and exactly saturated with normal nitric or hydrochloric acid (sulphuric or oxalic acid is, of course, not admissible). 17·5 c.c. are required; therefore 17·5 x 0·050 (the $\frac{1}{2000}$ of the molecular weight of $CaCO_3$) gives 0·875 gm. and as 1 gm. of substance only was taken = 87·5 per cent. of calcium carbonate.

PART II.

ALKALIMETRY AND ACIDIMETRY.

BOTH alkalis and acids when in pure aqueous solution can be determined with considerable accuracy by taking the specific gravity of the liquid at a definite temperature and referring to tables that have been carefully worked out for the purpose, e.g., those given on p. 52 of this book. In order to distinguish between free and combined acid or alkali volumetric methods only are available, the process being conducted by running into an acid or alkaline solution a standard solution of alkali or acid until it becomes exactly neutral. This is shown by means of an **indicator**, that is, a substance which, by its sudden change of colour, renders evident the transition from acidity to alkalinity, or vice versa. Most usually the indicator is added to the liquid to be titrated, and in this case it is called an **internal indicator.** In the case of dark-coloured liquids, however, this would clearly be inadmissible and an **external indicator** is used. This is spotted on a white porcelain plate and drops of the liquid that is being titrated are from time to time removed by a stirrer and brought into contact with the drops of indicator until the colour-change takes place that shows the reaction to have been completed. In some cases special test-papers, e.g., lacmoid paper, are used as an external indicator. Where great accuracy is desired two experiments should be made. The first gives an approximate result, which may be very nearly correct, and shows how much of the standard solution may safely be added to the solution before a single drop of it is removed to the plate. Then by continuing the addition cautiously but few drops of the liquid need be removed and the result obtained may be extremely accurate.

General Remarks on the Sensitiveness of Indicators. — Standard solutions of less than $^N/_{10}$ strength should rarely be used, since but few indicators are sensitive enough to give a sharp colour change with one or two drops of the solution. Iodo-eosin, in ethereal solution, is sufficiently sensitive to allow of the use of $^N/_{100}$ solutions. With $^N/_5$ and stronger solutions the sensitiveness of the three principal indicators is such that a single drop suffices to effect the change of colour; other indicators are mostly less sensitive. Alcohol lessens the sensitiveness of indicators and the presence of large amounts of it in solutions to be titrated should, therefore, be avoided as far as possible, especially when phenolphthalein is used. The most accurate results are obtained when titrations are conducted at ordinary temperatures. By dilution of the liquid the sensitiveness of the indicator is reduced. Since glass is attacked by alkalis, especially on boiling, with the liberation of both silicic acid and alkali, porcelain vessels should be used when liquids have to be boiled for some time to drive off carbon dioxide. Vessels made of "resistance glass" are now supplied and considerably minimize this danger. Glass is much more resistant towards acids. For accurate determinations with litmus and with phenol-phthalein in those cases where it is necessary to boil the solution to drive off CO_2, the solution should always be boiled in the presence of a slight excess of acid, then cooled, and the titration completed. When alkaloids in strong alcoholic solution are to be titrated, lacmoid is the best indicator.

The following statement by R. T. Thomson is worthy of note—"It is imperative that, before any indicator is used for a special purpose, its general similarity to another indicator should not be depended upon, but its property in the particular circumstances should be carefully tested".

The Use of a given Standard Solution with Different Indicators.—When various indicators are used in the titration of an acid liquid with a given standard alkali, or vice versâ, the results obtained are not identical, because more hydrogen or hydroxyl ions may be necessary in one case than in the other to produce a change of colour. For example, a solution of hydrochloric acid which is of exactly $^N/_5$ strength when standardized against pure sodium hydroxide, using methyl orange as indicator, is not accurately $^N/_5$ to phenol-phthalein, even when the titration is carried out with continual boiling to ensure the complete removal of CO_2 and all necessary precautions have been taken to secure the most accurate result. Hence, normal solutions should as far as possible always be standardized with the same indicator as they are subsequently to be used with in practice. A normal soda solution which has been made from caustic soda not quite free from carbonate should be standardized with methyl orange as indicator, then titrated with phenol-phthalein as indicator, and a factor worked out to convert burette readings in c.c. into their true values in terms of normal strength. The factor so obtained should be recorded on the stock bottle. It should be noted that in titrating acid with alkali the point of neutralization will be different from that observed with the inverse procedure, and it is therefore always necessary to finish the titration in the same sense as that in which the standard solution was itself adjusted, running in an excess and titrating back, if necessary.

1. **Litmus.**—Litmus is a blue dyestuff obtained from Roccella tinctoria. It is supplied in small bluish cubes, which contain, in addition to the colouring matter, varying amounts of calcium carbonate, gypsum, etc., and sometimes indigo as an adulterant. Litmus usually contains 4-5 per cent. of the actual colouring matter, which is called azolitmin and consists of the blue potassium salt of (red) azolitmic acid.

Sensitive Litmus Solution may be made by extracting the cubes with hot distilled water, added in successive portions, and uniting the extracts. The first extract, which contains excess of potassium carbonate, may be rejected. It is better simply to pour off the extracts, as filtration is a very tedious process. The combined extracts are then allowed to stand in a covered beaker for twenty-four hours and the liquid carefully poured off from the sediment. The solution is then divided into two parts and dilute hydrochloric or sulphuric acid added cautiously to one part, with constant stirring, till it becomes distinctly red. It is then mixed with the other half and a violet, or wine-red solution is obtained which is sensitive both to acids and alkalis. Reinitzer[1] recommends that the aqueous extract should be boiled for seven or eight minutes, and then neutralized with HCl, so that the wine-red colour remains even on further boiling. The solution is then cooled, and an equal volume of strong alcohol added.

Preliminary digestion of commercial litmus with alcohol is one of the best methods of purification. This removes the red colouring matter.

Digest the powdered litmus on the water bath with three successive portions of 90 per cent. alcohol (100 c.c. in all for 10 gm. litmus), decanting the alcohol after each digestion (of an hour). Extract the residue with hot water, and allow to stand and settle for a day or two. The clear extract at this stage is of sufficient purity and concentration (if not more than 100 c.c. of water has been used to 10 gm. litmus) for ordinary purposes. A higher degree of purity and sensitiveness, however, may be attained by concentrating the extract, acidifying with acetic acid (to decompose potassium carbonate), and evaporating to a syrupy consistency. Add a large excess of 90 per cent. alcohol, to precipitate the blue colouring matter. Filter, and dissolve the residue in hot water.

Free carbonic acid gives with litmus a pale port-wine colour, which renders indistinct the transition from the blue, produced by alkalis, to the red, produced by acids, or vice versâ. Hence the direct titration of alkali carbonates cannot be carried out in the cold, but the solution (in a porcelain dish) must be kept near the boiling-point and boiled for a minute or two every time a port-wine colour appears after an addition of standard acid. When the liquid again becomes blue on boiling, a further amount of acid is added, and the process continued as above until the solution remains distinctly and permanently red after boiling. Litmus, however, is much less sensitive in hot than in cold solutions (*vide infra*). For this reason the method of residual titration should be applied if accurate results are required. This is attained by adding an excess of standard acid, boiling the solution till all CO_2 is expelled, and, after cooling, titrating back with standard sodium or potassium hydroxide (free from carbonate).

In titrating acids with the aid of litmus it is in all cases advisable to continue the addition of standard alkali until a distinct blue colour is produced and not to stop at a violet coloration, because the transition from red to violet is not sharp, whilst that from violet to blue can be determined to a single drop.

Use of Litmus.—In addition to the three mineral acids, sulphuric, hydrochloric, and nitric, oxalic acid gives a sharp end reaction with litmus. Acetic acid also strikes well, except in the presence of much sodium acetate.

---

[1] *Analyst*, 1894, **19**, 255 (abstr.).

Litmus solution spoils when kept in closed vessels, owing, no doubt, to the development of anaerobic organisms. It should be kept in a bottle closed with a loosely fitting cork through which passes a delivery tube (fig. 25).

Litmus paper is made by dipping strips of calendered unsized paper in the solution and drying them; the solution used being rendered blue, red or violet as required.

Theory of the Action of Litmus.—The undissociated molecules of the litmus acids are red, the ions blue, and since the acids are weak, i.e. only slightly dissociated, a mixture of the two colours results in aqueous solution. On addition of hydrogen ions, that is acids, the litmus acids become practically undissociated, the blue anions disappear and the red colour of the undissociated molecules appears. To effect this change, however, a certain minimum concentration of hydrogen ions is necessary. Hence, very weak acids such as carbonic and hydrosulphuric have practically no action; acetic acid, on the other hand, acts quite distinctly, unless its ionization is so much decreased by the addition of sodium acetate that an insufficient amount of free hydrogen ions remains. When bases are added, salts of the litmus acids are formed which are largely dissociated, so that the blue colour of the ions is pronounced.

Azolitmin.—This is a specially pure litmus colouring matter, soluble in water. It is scarcely more sensitive than good litmus solution. The solution is made by dissolving 0·1 gm. in 100 c.c. of distilled water.

2. **Methyl Orange**[1] is *p*-dimethylaminoazobenzene *p*-sulphonic acid,

$$SO_3H \,.\, C_6H_4N \,.\, N \,.\, C_6H_4 \,.\, N(CH_3)_2$$

or its yellow sodium salt.

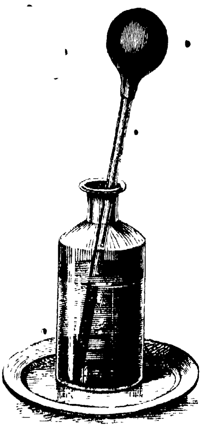

FIG. 25

Solution.—0·05 gm. in 100 c.c. of distilled water.

This valuable indicator was introduced by Lunge in 1881. Its great value lies in its almost complete indifference to carbon dioxide. A single drop of the above solution is usually sufficient for 100 c.c. of a colourless liquid, but in all cases no more of the indicator should be used than is necessary to impart to the solution a slight but distinct colour: if too much is added the colour change denoting the completion of the reaction will not be sharp. In fact, for titrating small volumes of liquid, say 30-40 c.c., even one drop of the above solution gives too strong a colour, a drop of a solution of half the strength being quite sufficient. The indicator is yellow in alkaline solution, red in acid solution.

Methyl orange is especially useful for the standardizing of any of the mineral acids by means of sodium carbonate in the cold. It acts admirably with ammonia and its salts. It must not, however, be used for organic acids. Hydrosulphuric, boric, arsenious, hydrocyanic, oleic, stearic, palmitic and carbolic acids, etc., have no effect on it. Nitrous acid gradually decomposes it, but this acid can be titrated with methyl orange either by adding a little more of the indicator just before neutralization, or by adding normal sodium hydroxide in excess and titrating residually with normal acid. All titrations with methyl orange should be conducted at ordinary temperatures and the solution to be titrated should not be too dilute. Moreover, since methyl orange is not very sensitive as compared with other indicators, standard solutions under $^{N}/_{5}$ strength should not be employed. With $^{N}/_{10}$ solutions, especially when carbonates are being titrated, there is a distinct brownish transition tint between the yellow and the pink, and results may be uncertain to the extent of 1 or 2 drops.

---

[1] Synonyms—Poirrier's Orange No. III, Helianthine and Tropaeolin D.

Some operators have used methyl orange in the titration of *alkaloids*, but in a series of very careful experiments, carried out by L. F. Kebler, it was found in some cases very defective (*J.A.C.S.*, Oct., 1895). Probably the most useful indicator for alkaloids is *Brazilin*, or a decoction of Brazil-wood; inapplicable in the presence of sulphuretted hydrogen or sulphurous acid. Dott recommends cochineal for alkaloids (*Ph. J.*, 1916, **96**, 368).

Note.—Although no difficulty is usually experienced in getting good methyl orange, every new supply purchased should be carefully tested. This is best done, if possible, by comparing it for sharpness of indication, under identical conditions of volume, temperature, etc., with a solution that has proved its excellence. Methyl orange should dissolve in cold water with no appreciable residue.

Ethyl Orange is similar to methyl orange, but is not quite so sensitive.

3. **Methyl Red** (*p*-dimethylaminoazobenzene-*o*-carboxylic acid) was introduced as an indicator in 1908 by Rupp and Loose,[1] who advocated its use because of its delicacy, and especially its value in the titration of ammonia and other comparatively weak bases, such as quinine. A 0 2 per cent. alcoholic or aqueous solution is used. It is faintly yellow in alkaline and neutral solutions, violet-red in acid solutions. Its behaviour under various conditions has been examined by a number of observers. R. T. Thomson and others find it much superior to methyl orange for the titration of ammonia, as for example in the Kjeldahl process. It is more affected by carbon dioxide than methyl orange is, but if the solution of carbonate is boiled after each addition of acid an excellent end-reaction is obtained. Generally, it may be taken to resemble litmus in its indications and, on account of its more decisive change in colour and the small amount of indicator required, is to be preferred to the latter. It is a particularly useful indicator at night, as the colour change is then very marked and easily discernible. According to Kay and Newlands,[2] with methyl red as indicator a single drop of $^{N}/_{100}$ acid is sufficient to decide the end-point. Lehmann & Wolff[3]

[1] *Analyst*, 1914, **38**, 518.

[2] *J.S.C.I.*, 1916, **35**, 445.

[3] *Ibid.*, 1917, **36**, 944.

state that the change from red to yellow is as sharp as that from yellow to red, and solutions standardised with phenolphthalein gave the same results when methyl red was used in place of the latter. The best results were obtained with 2 or 3 drops of a 0·1 per cent. solution in about 100 c.c. of liquid.

4. **Phenolphthalein** ($C_{20}H_{14}O_4$) is a weak acid, whose salts are red.

Solution.—0·5 gm. is dissolved in 50 c.c. alcohol and 50 c.c. distilled water added with constant stirring. The colourless solution so obtained is usually perfectly clear, but if not it should be filtered.

Phenolphthalein gives no colour with acid liquids, to which it is the most sensitive indicator, but becomes purple-red with the faintest excess of caustic alkali. The transition from red to colourless, however, is not so delicate as the inverse change, which is very distinct even in artificial light. Unlike methyl orange, an excess of this indicator is not harmful.

For the titration of hydroxides of the alkalis and alkaline earths phenolphthalein is undoubtedly the best and most sensitive indicator, if these are present alone in solution and free from carbonate. When alkali carbonates are present and are titrated in the cold the red colour remains until the whole of the carbonate has been converted into bicarbonate, e g.

$$Na_2CO_3 + HCl = NaCl + NaHCO_3$$

But when by further addition of acid the bicarbonate is decomposed and CO_2 set free, the latter destroys the red colour.

This indicator is useless for the titration of free ammonia or its compounds, or for the fixed alkalis when salts of ammonia are present; except with alcoholic solutions, in which case caustic soda and potash displace the ammonia in equivalent quantities at ordinary temperatures and the indicator forms no compound with the ammonia. Unlike methyl orange, this indicator is especially useful in titrating organic acids—oxalic, acetic, citric, tartaric, etc.

One great advantage possessed by phenolphthalein is that it may be used in alcoholic solutions or in mixtures of alcohol and ether[1] and, therefore, many organic acids insoluble in water may be titrated by its help; in addition to this it may be used to determine the acid combined with many organic bases, such as morphine, quinine, brucine, etc., the base having no effect on the indicator.

Reinitzer[2] found that phenolphthalein was three times more sensitive in a cold than in a hot solution.

Sodium silicate cannot be titrated alone with any degree of accuracy with phenolphthalein as indicator, the change of colour being gradual, not sharply defined. By adding to the solution sodium chloride, however, good results are obtained in accordance with the equation $Na_2SiO_3 + 2HCl = 2NaCl + H_2SiO_3$.

---

[1] H. N. and C. Draper (*C. N.*, **55**, 143) have shown that this indicator is rapidly decomposed by atmospheric carbonic acid, which is more readily absorbed by alcohol than by water. Fortunately this is less the case with hot solutions than with cold; titration of this kind should therefore be quickly done, and with not too small a quantity of the indicator

[2] *Analyst*, 1894, **19**, 256.

For the behaviour of this indicator with phosphoric acid, *vide* under "Phosphoric Acid".

Mixture of Phenolphthalein and Methyl Orange.—This is a neutrality indicator made by dissolving 5 gm. of the first and 1 gm. of the latter in a litre of 50 per cent. alcohol. The neutral point is shown by a lemon-yellow colour. The slightest excess of either acid or alkali shows in turn pink and bright red.

5. **Cochineal Solution.**—This indicator possesses the advantage over litmus that it is not so much modified in colour by the presence of carbonic acid and may be used by gas-light. It may also be used with the best effect with solutions of the alkaline earths, such as lime and baryta water; the colour with pure alkalis and earths is especially sharp and brilliant. The solution is made by digesting 1 part of crushed cochineal with 10 parts of 25 per cent. alcohol. Its natural colour is yellowish-red, which is turned to violet by alkalis; mineral acids restore the original colour. It is not so easily affected by weak organic acids as litmus, and therefore for these acids the latter is preferable. It cannot be used in the presence of even traces of iron or alumina compounds or acetates, which fact limits its use. Carminic acid is the true sensitive element in cochineal, and it is sometimes preferable to cochineal in very delicate operations.

6. **Phenacetolin.**—This indicator is slightly soluble in water but readily in 50 per cent. alcohol, and a convenient strength is 2 gm. per litre. The solution is greenish brown, giving a scarcely perceptible yellow with caustic soda or potash when a few drops are used with ordinary volumes of liquid. With ammonia and the normal alkali carbonates it gives a dark pink, with bicarbonate a much more intense pink, and with mineral acids a golden yellow. This indicator may be used to determine the amount of caustic potash or soda in the presence of their normal carbonates if the proportion of the former is not very small, or of caustic lime in the presence of carbonate, but no ammonia must be present.

Practice, however, is required with solutions of known composition, so as to acquire knowledge of the exact shades of colour.

7. **Turmeric Paper.**—Pettenkofer, in his determination of carbonic acid by baryta water, prefers turmeric paper as an indicator. For this purpose it is best prepared by digesting pieces of the root, first in repeated small quantities of water to remove a portion of objectionable colouring matter, then in alcohol, and dipping strips of calendered unsized paper into the alcoholic solution, drying and preserving them in the dark. Or 1 part of powdered turmeric may be digested for about an hour with 6 parts of weak alcohol (3 volumes of alcohol to 1 of water) in a covered flask, with occasional shaking. The filtered liquid (tincture of turmeric) is used to prepare turmeric paper. Both liquid and paper should be protected from light.

Thomson, in continuance of his valuable experiments on various indicators, found that turmeric paper is of very little use for ammonia, or the alkali carbonates, or sulphides or sulphites, but he prepared a special paper of a light red-brown colour by dipping it into tincture of turmeric rendered slightly alkaline by caustic soda. If this paper is wetted with water the colour is intensified to a dark red-brown; when partly immersed in a very dilute solution of an acid, the wetted portion becomes bright yellow, while immediately above this a moistened dark red-brown band is formed and the upper dry portion retains its original colour. This appearance only occurs in the titration of a comparatively large proportion of an acid, when the latter is nearly all neutralized, and thus serves to indicate the near approach to the end-reaction. When neutral or alkaline, the colour of the immersed portion of paper is simply intensified as already described. This intensification is quite as decided as a change of tint. This red-brown paper is as sensitive as phenolphthalein for the titration of citric, acetic, tartaric, oxalic and other organic acids by standard soda or potash, and may be used for highly coloured solutions. It is also available, like phenolphthalein, for the determination of small quantities of acid in strong alcohol.

8. **Rosolic Acid, Corallin, or Aurine** ($C_{20}H_{16}O_3$) is soluble in 60 per cent. alcohol, and a convenient strength is 2 gm. per litre. Its colour is pale yellow, unaffected by acids, but turning to violet-red with alkalis. It possesses the advantage over litmus and the other indicators that it can be relied upon for the neutralization of sulphurous acid with ammonia to normal sulphite (Thomson). Its delicacy is sensibly affected by salts of ammonia and by carbonic acid. It is excellent for all the mineral, but useless for the organic acids, excepting oxalic.

9. **Lacmoid.** This indicator is a product of resorcin, and is therefore somewhat allied to litmus; nevertheless, it differs from it in many respects, and has a pronounced and valuable character of its own, especially when used in the form of paper. Lacmoid is soluble in dilute alcohol, and the indicator is made by dissolving 3 gm. to the litre.[1]

10. **Lacmoid Paper.**—This is prepared by dipping slips of calendered unsized paper into the blue or red solution, and drying them.

Thomson states that, in nearly every particular, lacmoid paper, either blue or red, is an excellent substitute for methyl orange, and may be employed in titrating coloured solutions where the latter would be useless. Solution of lacmoid, on the other hand, is not so valuable as the paper, inasmuch as it is more easily affected by weak acids such as carbonic, boric, etc. See p. 40.

11. **Congo Red.**—Dissolve 0·5 gm. in 90 c.c. of water and 10 c.c. of alcohol; or a 1 per cent. solution is made in 30 per cent. alcohol, and 1 drop is added to 10 c.c. The alcohol is present to prevent the precipitation of the blue acid by acids. The change from blue to red is easier to observe than that from red to blue. This indicator is much used for titrating aniline bases and alkaloids. It is affected by neutral salts, especially by those of the alkaline earths, and also by proteins.

---

[1] This solution is rendered much more effective as an indicator if Forster's suggestion is adopted, namely, the addition of about 5 gm. of napthol green to a litre of the solution. The effect is to produce a more decided blue colour with alkalis than is given by lacmoid alone.

SUMMARY OF THOMSON'S RESULTS SHOWING THE BEHAVIOUR AND SENSITIVENESS OF THE PRINCIPAL INDICATORS.

	Litmus.	Lacmoid.	Aurin.	Methyl Orange.	Phenacetolin.	Phenolphthalein.
Sensitiveness . .	0·05	0·01	0·01	0·05	0·01	0·01
Hot solutions . .	Available.	Available.	—	—	—	—
Alkali carbonates .	Indefinite.	Indefinite.	Indefinite.	Alkaline.	Red colour.	Alkaline.
Alkali bicarbonates .	do.	do.	do.	do.	—	Neutral.
Alumina . . .	do.	Alkaline.	do.	do.	Neutral.	do.
Ammonia . . .	Available.	Available.	Available.	Available.	Available.	Not available.
Ammonium salts .	Not affected.	Not affected.	Less sensitive.	Less sensitive.	Not affected.	do.
Arsenic acid . .	Indefinite.	Monobasic.	Indefinite.	Monobasic.	Monobasic.	Dibasic.
Arsenious acid . .	Neutral.	Neutral.	do.	Neutral.	Neutral.	Indefinite.
Boric acid . . .	Indefinite.	Indefinite.	do.	do.	Indefinite.	do.
Carbon dioxide .	do.	do.	do.	Not affected.	Colour changed.	do.
Hydrogen sulphide .	do.	Decolorized.	do.	do.	Not affected.	do.
Hydrosulphides .	do.	Not available.	—	Alkaline.	—	Neutral.
Neutral alkali salts .	Not affected.	Not affected.	Not affected.	Less sensitive.	Not affected.	Not affected.
Oxalic acid . .	Available.	Not available.	Available.	Not available.	Not available.	Available.
Phenol . . .	Neutral.	Neutral.	Neutral.	Neutral.	Neutral.	Indefinite.
Phosphoric acid . .	Indefinite.	Monobasic.	Indefinite.	Monobasic.	Indefinite.	Dibasic.
Potassium nitrite .	Neutral.	—	Neutral.	Destroyed.	Neutral.	Neutral.
Silicic acid . .	do.	Neutral.	do.	Neutral.	do.	Not available.
Sodium thiosulphate .	do.	do.	do.	do.	do.	Neutral.
Sulphides . . .	Alkaline.	Not available.	—	Alkaline.	Alkaline.	Alkaline.
Sulphites . . .	Indefinite.	Alkaline	Neutral.	do.	Not available.	Neutral.
Acid sulphites . .	do.	Neutral.	Acid.	Neutral.	do.	Acid.

In the above table the "sensitiveness" is measured in c.c. of decinormal acid required to produce a distinct change of colour when the volume of the liquid is 100 c.c. The term "Indefinite" is used to mean that the colour change is not sufficiently sharp to be available in analysis.

12. **Extra Sensitive Indicators.**—Mylius and Förster[1] describe a series of experiments on the determination of minute traces of alkali and the recognition of the neutrality of water by means of an ethereal solution of iodeosin or erythrosin. This body is a derivative of fluorescin, and occurs plentifully in commerce as a dye for fabrics and paper. The commercial material is purified by solution in aqueous ether, and the filtered solution is shaken with dilute caustic soda, which removes the colour; the latter is then precipitated with stronger alkali. The salt is then filtered off, washed with spirit and finally recrystallized from hot alcohol. The indicator used by the operators was made by dissolving 1 decigram of the dry powder in a litre of aqueous pure ether. The ether of commerce is purified and rendered neutral by washing with weak alkali, afterwards with pure water, and keeping the ether over pure water. The indicator so prepared is quite useless for the ordinary titration of acids and alkalis; its chief use is for the detection and measurement of very minute proportions of alkali such as would occur in water kept in glass vessels, or the solubility of calcium or other earthy carbonates in water free from carbonic acid, or in the use of millinormal solutions of alkalis and acids, also the neutrality of so-called pure salts or water. The method of using the indicator is to shake up, say, 20 c.c. with 100 c.c. of the liquid to be examined, when, if alkali is present, a rose colour will be communicated to the layer of ether which rises to the top. The indicator may be used in conjunction with millinormal standard solutions, or colorimetrically, like the well-known Nessler test. Further details of its use are described in the contributions mentioned. Another similar indicator is mentioned by Ruhemann, viz., the imide of dicinnamylphenylazimide.[2] This material gives a violet rose colour with the most minute traces of alkali such, for instance, as would appear from merely heating alcohol in a test tube,—the faint trace of alkali thus derived from the glass being sufficient to cause a rapid development of colour.

There is a large number of other indicators, either in solution or as test papers, and where necessary these will be mentioned.

THEORY OF INDICATORS.

BEFORE proceeding to give an account of the Theory of Indicators, a short summary of the Ionic Theory may be useful.

The term "ions" we owe to Faraday, who so named the component parts, consisting of elements or groups of elements, into which an electrolyte was decomposed by a current of electricity. Where the current entered the liquid—the **anode**—the electronegative constituents (halogens and acid radicles like NO_3, SO_4) or **anions** appeared, while hydrogen and the metals apparently move with the current and are liberated as **cations**—the electropositive constituents—at the cathode. These ions, then, are the true constituents of salts. Symbolically, anions are usually represented by a dash (′) placed immediately after the chemical formula and cations, in like manner, by a dot (·). Thus,

---

[1] *Berichte*, **24**, 1482; also *C. N.*, **64**, 228, *et seq.*

[2] *J. C. S. Trans.* **61**, 285.

Na· represents the sodium ion as present in, e.g. an aqueous solution of salt, and Cl′ denotes the chlorine ion.

Multivalent ions are marked with as many dots and dashes as correspond to their valencies or electric charges.

Williamson and Clausius suggested long ago that it was highly probable that electrolytes existed, to a certain extent at least, as free ions; but it is to Arrhenius that the Ionic Theory, as we now know it, is principally due. According to this chemist salts do not exist entirely as such in aqueous solution, but are dissociated more or less completely into their constituents or ions. The term "salt" includes both acids and bases, acids being salts of hydrogen and bases salts of hydroxyl. Thus, in an acid we have an anion and hydrogen, H·, while in a base we have a cation and hydroxyl OH′. Water, the compound of hydrogen and hydroxyl, is ionized to but a very slight extent: hence it follows that water is always formed when the two constituent ions meet in any liquid.

Faraday and others had noticed that during electrolysis of a salt the salt became more concentrated in the neighbourhood of one pole, and more dilute round the other. The true explanation of this observation was found by Hittorf (1853) in the fact that the two ions do not generally move at an equal rate. If they do, there is no such alteration of concentration. But in the more numerous cases, where their rate of motion is different, the salt concentrates round the pole to which the more rapidly moving ion is travelling. Hittorf also pointed out that compounds, solutions of which are good conductors of electricity, are precisely those which are most susceptible of chemical reaction. In later years this observation has proved one of great importance. It has been found that electrolytic dissociation and electrolytic conductivity are so closely related that conclusions can be drawn with respect to the former by measuring the amount of the latter under given conditions. The degree of dissociation is deduced from the osmotic pressure of the solution, and from its electric conductivity at different dilutions. The osmotic pressure is determined (1) directly, (2) from the raising of the boiling point, and (3) from the depression of the freezing point of the solvent by the presence of the dissolved substance or solute.

In aqueous solutions of electrolytes the ions are usually partly combined and partly free. Of the different kinds of salts neutral ones are the most strongly ionized; their aqueous solutions of medium concentration usually contain much more than half the total salt in the condition of free ions. In the case of neutral salts, also, the dissociation always increases as the solution becomes more dilute. Hence the properties of a dilute solution of a salt are mainly dependent upon those of its free ions. Neutral salts are all ionized to about the same extent, however strong or weak their acid may be.

Salts containing univalent ions are the most dissociated, the dissociation decreasing as the valency of the ions increases.

Acids and bases are classified as strong or weak according to the degree of their ionization, the strongest in each case being those most completely ionized. The strong acids, whose ionization is of the same order as that of neutral salts are the halogen hydrides (except hydrofluoric acid, which is only moderately ionized), nitric, chloric, perchloric, sulphuric, and the polythionic acids.

Moderately strong acids comprise phosphoric, sulphurous and acetic acids, which are not ionized beyond about 10 per cent. under ordinary conditions.

The weak acids are carbonic, hydrosulphuric, hydrocyanic, silicic and boric acids, -in all of which the ionization is under 1 per cent.

The principal strong bases are the hydroxides of the alkali and alkaline earth metals and of thallium, and also of the organic quaternary ammonium compounds. All these are ionizable to about the same extent as neutral salts.

The **Law of Mass-action,** as propounded in its most general form by Wenzel in 1777, is that the strength of chemical action is proportional to the concentration of the acting material, this being determined by the amount in unit volume. If two substances act on each other, the action is proportional to the relative amount of each, and will be zero if the amounts of acting bodies is zero, and therefore it is proportional to the product of the two. Further, the action will depend on the nature of the substances, on the temperature, and on other circumstances; these influences can be expressed by a factor, hence the "force" of the chemical affinity can be represented by the expression kpq, if k is the factor, and p and q are the acting masses. But this action is balanced by forces acting in opposition to the formation of the new system, which tend to restore the primary condition of the substances. If the substances formed by the original reaction are p' and q', and the new factor k', equilibrium will be established when $kpq = k'p'q'$. Although it is not possible to calculate the actual amount of the "chemical forces," it is possible to calculate their ratio, by knowing the position of equilibrium, when the reaction has gone as far as it will, under a given set of conditions. The result of such calculations gives the relative velocities of chemical reactions.

In solutions of electrolytes a state of equilibrium subsists between the ions of the electrolytes and the non-dissociated portion, which can be expressed in the form of an equation. Thus in the case of a binary electrolyte C, which can break up into the ions $A^{\cdot}$ and B', if a represent the concentration of the anion, b that of the cation, and c that of the non-ionized portion of a given solution, then the following simple relation holds good,

$$ab = kc$$

where k is a constant depending upon the nature of the substance and to a slight extent upon its temperature.

Two neutral salts exert almost no action upon each other, because both they themselves and the possible resultant new salts produced by their double decomposition are all strongly ionized, and the ions remain substantially in their original condition. Thus a solution of potassium chloride consists chiefly of the ions $K^{\cdot}$ and Cl', and one of sodium nitrate of the ions $Na^{\cdot}$ and NO'_3, and these conditions are not altered by mixing the solutions together.

Further, this resulting solution is necessarily identical with one made from corresponding quantities of sodium chloride and potassium nitrate, since the former contains the same ions in the same free state as the latter.

When solutions of acids and bases are mixed, an energetic reaction takes place, the hydrogen and hydroxyl ions uniting to form water, while the other two ions of the resulting salt remain in the solution in the free state.

Remembering that all neutral salts are ionized to about the same extent, we can now understand what takes place when a strong acid is added to the salt of a weak one. Both of these being strongly ionized, the anions of the salt unite with the hydrogen of the acid to form a second acid, which is but little ionized, seeing that we started with the salt of a weak acid, i.e. of an acid which itself undergoes only slight ionization. At the same time the anion of the added (strong) acid remains along with the cation of the original salt; in other words, the solution now contains (the ions of the) salt formed by the production of the weak by means of the strong acid Thus the true cause of the reaction lies in the tendency of the ions of the weak acid to pass into the nonionized condition. This reaction becomes less complete as the newly formed acid is more strongly ionized, and should the latter be ionizable to the same extent as the added acid, no reaction would take place.

APPLICATION OF THE IONIC THEORY TO INDICATORS.

Artificial indicators are either very weak organic acids or weak bases, and their behaviour is such that in solution their colour in the nonionized state differs from that which they exhibit in the ionic condition. It seems, also, that in addition to a change in the ionic condition of an indicator there are cases where the change of colour is associated with tautomeric change.

Strong acids or bases are inadmissible as indicators, since they ionize too strongly while in the free state and would, therefore, show no change of colour on neutralization. For, when a strong acid is neutralized, only its free hydrogen ions form water with the hydroxyl of the base, the anion remaining unaltered. A weak acid, on the other hand, exists for the most part as undissociated molecules in solution and not as ion, the ions being produced only after neutralization, i.e. after the conversion of the acid into neutral salt, seeing that the neutral salts of even weak acids undergo very complete ionization.

Methyl Orange is an acid of medium strength. Its ions are:—

$$(CH_3)_2\,N\,.\,C_6H_4\,.\,N:N\,.\,C_6H_4\,.\,SO'_3 \text{ and } H^{\cdot}$$

of which the former exhibits a yellow colour. The undissociated salt is, however, red; so that in an aqueous solution the colour observed is an intermediate one. Addition of a trace of strong acid (i.e. increase of $H^{\cdot}$ ions) diminishes the very slight dissociation, and the red colour of the undissociated substance predominates.

In the titration of a basic liquid, to which a drop or two of methyl-orange has been added, the colour change is from yellow to red when a strong acid is added—the yellow colour being due to the ionization of the indicator which is brought about by a very slight increase of concentration of the hydroxyl (OH′) ions.

Where, however, a weak, i.e. only slightly ionizable, acid is added, the quantity of H· ions on passing the point of neutralization is too small to allow of the formation of visible amount of non-ionized compound,—hence no colour-change is observed. Accordingly, this indicator is useful only when strong acids are being dealt with. For bases, both strong and weak, it is, however, the proper indicator to use, as its decided acid nature permits of its forming salts with very weak bases, and those salts are not hydrolysed to any extent by water.

Phenolphthalein is a very weakly acid indicator, which is colourless both in acid and in neutral solution, but intensely red in the presence of caustic alkali, i.e. the undissociated molecule is colourless, but when ionized it becomes red. It can be used for the determination of weak acids such as carbonic acid, organic acids and H_2S, because the acid, if present in the slightest excess, will give up its hydrogen to it, thus producing the change of colour that accompanies the passage from the ionic state to that of the non-ionized molecule. It can only be employed with strong bases, however, as with weak ones it forms salts incompletely, the latter being decomposed by hydrolysis with the water present. Ammonia, for example, is too weak a base in itself to yield a normal salt with phenolphthalein in very dilute solution, i.e. to give the free ions of the salt. In fact, a distinct excess of ammonia is required to overcome the hydrolytic action of the water; hence, the change of colour in presence of salts of ammonia is anything but sharp, and only apparent when a considerable excess of base is present.

For titration of weak acids it is admirable as an indicator, a strong base (barium hydroxide by preference) being used. For alkalimetry it can be used only when a strong base is to be determined. But concentrated solutions must be diluted before titration, as they destroy the red colour of the indicator and it cannot afterwards be restored by dilution.

Summing up, we may say that for the titration of weak acids a moderately ionized indicator is alone of use, while weak bases require as feebly basic indicators as possible.

For further information on these subjects the reader is referred to Ostwald's *Scientific Foundation of Analytical Chemistry*, translated by G. McGowan; Ramsay's *Introduction to the study of Physical Chemistry*, and papers by Dr. J. T. Hewitt on the "Constitution of Indicators" (see *Analyst*, 1908, **33**, 85, etc.)—all of which have been laid under contribution in the preparation of this section.

PREPARATION OF THE NORMAL ACID AND ALKALI SOLUTIONS.

It is quite possible to carry out the titration of acids and alkalis with only one standard liquid of each kind; but it frequently happens that standard acids or alkalis are required in other processes of titration besides mere saturation, and it is therefore advisable to have a variety.

Above all things it is absolutely necessary to have at least one standard acid and one standard alkali prepared with the most scrupulous accuracy to use as foundations for all others.

It is preferable to use sulphuric acid for the normal acid solution, inasmuch as there is no difficulty commercially in obtaining the purest acid. The normal acid made with it is totally unaffected by boiling, even when of full strength, which cannot be said of either nitric or hydrochloric acid. Hydrochloric acid is, however, generally preferred by alkali makers, owing to its giving soluble compounds with lime and similar bases. Nitric and oxalic acids are also sometimes convenient.

Sodium carbonate, on the other hand, is to be preferred for the standard alkali, because it may readily be prepared in a pure state, or may easily be made from pure sodium bicarbonate as described further on. Differences of opinion exist among chemists as to the best substances to be used as standards in preparing the various solutions used in alkalimetry and acidimetry. My experience satisfies me that, although many of these modifications may serve very well as controls, there is no more reliable standard than pure sodium carbonate.

The chief difficulty with sodium carbonate is that, with litmus as indicator, the titration must be carried on at a boiling heat in order to get rid of CO_2, which obscures the pure blue colour of the indicator, notwithstanding the alkali may be in great excess. This difficulty is now set aside by the use of methyl orange. In case the operator has not this indicator at hand, litmus or phenolphthalein gives perfectly accurate results if the saturation is first conducted by rapidly boiling the liquid for a minute after each addition of acid, until the point is reached when one drop of acid in excess gives a change of colour which is not altered by further boiling. This is used as a preliminary test, but as titrations are usually conducted at ordinary temperatures the final adjustment should be made by adding in the second trial a moderate excess of the acid, then boiling to get thoroughly rid of CO_2, rapidly cooling the liquid, and titrating back with an accurate standard alkali. A slight calculation will then give the figures for adjustment. If great accuracy is required this boiling must not take place in glass flasks, but in vessels of porcelain, platinum, or silver, as even Jena glass is affected by boiling alkaline solutions.

As has previously been said, these two standard acid and alkali solutions must be prepared with the utmost care, since upon their correct preparation and preservation depends the verification of other standard solutions.

The best method of preparing sodium carbonate for standardizing sulphuric or hydrochloric acid is to half fill a platinum basin with pure sodium bicarbonate in powder ($NaHCO_3$).[1] Place it in an air bath already heated to about 200° C., and raise the temperature to 270–80°, but not more than 300° C. Let it remain at this temperature for half an hour, then cool it in a desiccator, and before it is quite cold transfer it to a warm, dry, stoppered tube or bottle, out of which, when cold, it may be weighed rapidly as wanted. The carbonate so produced will be free from lumps and easily soluble in cold distilled water. To standardize the diluted acid, about 2 or 3 gm. of carbonate should be quickly weighed, dissolved in about 80 or 100 c.c. of water, 2 drops of methyl orange solution added, and the operation completed by running the acid of unknown strength, in small quantities at a time, from a burette divided into $\frac{1}{10}$ c.c. into the soda solution until exact saturation is effected.

---

[1] If there is any doubt as to the purity of the bicarbonate, it should be shaken with twice its weight of ice-cold water (preferably saturated with CO_2), transferred to a filter, washed on the filter with the same weight of water as before, and dried on the water-bath.

A second trial should now be made, but preferably with a different weight of the salt. The saturation is carried out precisely as at first. The data for ascertaining the exact strength of the acid solution by calculation are now in hand.

A strictly normal acid should at 15° C. exactly saturate sodium carbonate in the proportion of 100 c.c. to 5·3 gm.

Suppose that 2·46 gm. carbonate required 41·5 c.c. of the acid in the first experiment, then

$$2{\cdot}46 : 5{\cdot}3 :: 41{\cdot}5 : x = 89{\cdot}4 \text{ c.c.}$$

Again: 2·153 gm. carbonate required 36·3 c.c. of acid, then

$$2{\cdot}153 : 5{\cdot}3 :: 36{\cdot}3 : x = 89{\cdot}4 \text{ c.c.}$$

The acid may now be adjusted by measuring 890 c.c. into the graduated litre cylinder, adding 4 c.c. from the burette, or with a small pipette and filling to the litre mark with distilled water.

Finally, the strength of the acid so prepared must be proved by taking a fresh quantity of sodium carbonate. If the measuring instruments all agree, and the operations are all conducted with due care, a drop or two in excess of either acid or alkali in 50 c.c. should suffice to reverse the colour of the indicator.

The adoption of sodium carbonate as a standard for preparing normal acid solutions is strongly recommended in Lunge's Report to the International Congress of Applied Chemistry.[1] From the acid so standardized a corresponding normal caustic alkali may be made, and from that a normal oxalic acid, and from that a decinormal permanganate solution.

Sodium Thiosulphate as Standard in Alkalimetry (W. Feld).[2]—When excess of mercuric chloride is added to a solution of thiosulphate the latter is oxidized in accordance with the following equation:

$$Na_2S_2O_3 + 2HgCl_2 + H_2O = Hg_2Cl_2 + Na_2SO_4 + 2HCl + S.$$

It is suggested therefore, that sodium thiosulphate, which is obtainable commercially in a state of great purity, affords one of the best available standards for controlling standard alkali solutions. It is doubtful, however, whether the method could be used for alkali solutions of strength greater than decinormal, as the following considerations will show. By the above equation 248·22 gm. of crystallized thiosulphate ($Na_2S_2O_3$, $5H_2O$) liberate 2 × 36·468 gm. HCl equivalent to 2 × 40·008 gm. NaOH, or 124·11 gm. crystallized thiosulphate are equivalent to 1 litre of $^{N}/_{1}$. NaOH. Hence 12·411 gm. crystallized thiosulphate = 1 litre $^{N}/_{10}$ NaOH. The author recommends that about 0·5 gm. of thiosulphate be accurately weighed out, dissolved in water, and the solution added to 40 c.c. of a cold saturated solution of mercuric chloride. Excess of mercuric chloride is essential, as otherwise black mercuric sulphide separates. Five minutes are allowed for the reaction to complete itself and then about 30 c.c. of 4N ammonium chloride solution is added to prevent the precipitation of yellow mercuric oxide by the caustic alkali, which would mask the colour of the indicator. Methyl orange is added, and the titration with the caustic alkali proceeded with. 0·5 gm. of the thiosulphate would require about 40 c.c. $^{N}/_{10}$ NaOH to be added. The error of the method is stated to be ± 0·05 c.c. $^{N}/_{10}$ alkali.

---

[1] *Z. f. angew. C.*, 1903, **24**, 560, also *Analyst*, 1903, **28**, 307.

[2] *Z. a. C.* 1911, **29**, 1161 and *Analyst* 1911, **36**, 435.

Potassium bi-iodate,[1] $KH(IO_3)_2$, an acid salt, which can easily be obtained in a state of great purity, has been recommended for standardizing normal potassium hydroxide, using phenolphthalein as indicator. 3·8995 gm. dissolved in water require exactly 10 c.c. of the alkali solution.

Sodium oxalate, prepared as recommended by Sörensen,[2] is a reliable and accurate standard for acidimetry. It is converted into sodium carbonate by moderate ignition.

Sodium oxalate can readily be obtained free from water of crystallization, according to Sörensen, and is not hygroscopic. As prepared according to his directions, by preparation with alcohol and drying at 240°, it may be used either directly or after a few hours' heating in the steam oven. Some of the salt is carefully weighed in a platinum crucible, which is then covered with the lid, and while supported in a hole in a piece of asbestos cardboard heated for 15-30 mins. over a small gas flame until the sodium carbonate formed just begins to fuse; towards the end of the operation the lid is moved aside so as to cover about one-half of the crucible and thus bring about the complete combustion of the carbon formed. The ignition of the salt with complete combustion of the carbon, which Sörensen himself regards as absolutely necessary, doubtless requires considerable care in order to prevent loss during the process The resulting carbonate is then transferred to a Jena beaker, dissolved in water, methyl orange added and the acid solution titrated.

10 c.c. $^{N}/_{10}$ acid correspond to 0·06705 gm. of sodium oxalate and 0·1 gm. of sodium oxalate corresponds to 14·91 c.c. of $^{N}/_{10}$ acid.

The following have also been proposed as standards:—

Potassium bitartrate, $KHC_4H_4O_6$. 3·763 gm. = 20 c.c. normal caustic potash solution, using phenolphthalein as indicator, and boiling repeatedly during the titration.

Succinic acid, $C_2H_4(COOH)_2$, using phenolphthalein as indicator; arsenious acid,[3] mercuric oxide,[4] and acid potassium phthalate,[5] $KHC_8H_4O_4$, an anhydrous, non-hygroscopic, stable and colourless salt, readily prepared from phthalic anhydride.

---

[1] Meinecke, *C. Ztg.*, **19**, 2.

[2] *Z. a. C.* 1903, **42**, 333, and *Analyst* 1903, **28**, 306

[3] Menzies and McCarthy, *J. A. C. S.*, 1915, **37**, 2021.

[4] Rosenthaler and Abelmann, *Ph. J.*, 1913, **91**, 144

[5] F. D. Dodge, *J. Ind. and Eng. Chem.*, 1915, **7**, 29, W. S. Hendrixson, *J. A. C. S.*, 1915, **37**, 2352; *Analyst*, 1915, **40**, 171 and 509.

. Normal Sodium Carbonate

53 gm. Na_2CO_3 per litre.

This solution is made by dissolving crystals of pure sodium carbonate, then ascertaining its strength by a correct normal acid at 15°, and adjusting its volume so that it corresponds exactly with the normal acid. Absolutely pure anhydrous sodium carbonate is difficult to find in commerce, and even if otherwise pure is generally contaminated with insoluble dust contracted in the process of drying. The solution does not keep well, as it rapidly attacks glass.

2. Normal Potassium Carbonate.

69·1 gm. K_2CO_3 per litre.

This solution is sometimes, though rarely, preferable to the soda salt, and is of service for the determination of combined acids in certain cases where, by boiling with this reagent, an interchange of acid and base takes place.

It cannot be prepared by direct weighing of the potassium carbonate, and is therefore best made by titrating a solution of unknown strength with strictly normal acid and adjusting as described above.

3. Normal Sulphuric Acid.

49·038 gm. H_2SO_4 per litre.

About 30 c.c. of pure sulphuric acid of sp. gr. 1·840, or thereabouts, are mixed with three or four times the volume of distilled water and allowed to cool, then put into the graduated cylinder and diluted up to about a litre at the proper temperature. The solution may now be titrated with sodium carbonate, as previously described, and accurately adjusted.

Or thus: Suppose that two litres of normal sulphuric acid are required. Counterbalance a beaker with shot on a rough balance and *weigh* into it 104 gm. of concentrated sulphuric acid. This is easily done by putting a 5 gm. weight on the pan with the beaker and pouring the acid in a thin stream till it is in excess of the weight, then removing the 5 gm. weight and adding the acid drop by drop till it is the correct weight or a little more. Then pour it into a litre flask containing about 500 c.c. of distilled water, rinse the beaker several times with water, adding the rinsings to the flask, and after shaking the flask allow it to stand several hours till it has acquired the temperature of the laboratory. Now make up to the mark with distilled water, mix, and transfer to the stock bottle. Fill up the litre flask with distilled water and pour this also into the stock bottle. Mix thoroughly and we have a solution rather stronger than normal. Next weigh out ·06 gm. of sodium carbonate and dissolve in about 30 c.c. of water in a Jena beaker. Fill a burette with the acid and run carefully into the soda solution, to which a drop or two of methyl orange has been added, until a pink colour remains after well stirring. Let 18·9 c.c. of the acid be required (instead of 20 for normal). Then the solution requires the addition of 1·1 c.c. of water for every 18·9 c.c. It measures 2000 − 18·9 = (say) 1981 c.c.

$$\therefore\ 18{\cdot}9 : 1981 = 1{\cdot}1 : x.$$

$$x = 1153{\cdot}$$

Now, as an approximation to correct strength with a certainty of being on the right side, pour carefully 110 c.c. of water into the stock bottle, run the liquid from the burette into it, mix thoroughly, fill up the burette twice and then titrate again, using 2·12 gm. of the alkali and running the acid into it *slowly*. Suppose that exactly 39·9 c.c. are required (instead of 40). The solution now measures 1981 + 110 − 40 = 2051 c.c. and the amount of water to be added is

$$39·9 : 2051 = 0·1 : x.$$
$$x = 5·1 \text{ c.c.}$$

Add this quantity of water to the bulk, mix thoroughly as before, and the solution should be of exactly normal strength, and should be proved to be so by a final titration with 2·12 gm. of sodium carbonate as before.

If the standard solution has inadvertently been made too weak, it may be rectified as follows. Suppose that, in the above example, 1·06 gm. of sodium carbonate required 20·6 c.c. of the acid solution instead of 20 c.c. Thus, 20·6 c.c. of the solution are equivalent to 20 c.c. of normal strength, and 1 c.c. of the former $= \frac{20·0}{20·6} = 0·97087$ c.c. of normal acid. Two litres contain 0·97087 × 98·076 = 95·220 gm. of H_2SO_4 instead of 98·076 gm. for normal strength. Hence, 98·076 − 95·220 = 2·856, say 2·9 gm. have to be added. This amount is accordingly weighed out in a small counterpoised beaker, which is then filled up with the weak solution, emptied into the bulk, again rinsed out in the same way, the whole well mixed, and the solution again tested as before.

In the foregoing directions for the preparation of standard acid and alkali it is evident that, with the exception of control by the rather doubtful method of precipitation of the sulphuric acid by barium, the responsibility for an accurate acid solution is thrown upon the sodium carbonate, and though my experience has been that with proper care this is quite reliable, it is plain that any other means of getting at the accurate strength of the sulphuric acid will be acceptable. This is now, owing to the elaborate and careful experiments of Pickering on the specific gravities of solutions of sulphuric acid of various strengths, rendered quite possible.[1]

It is true that the conditions under which the working strength of the acid is obtained are very stringent, and need the utmost care in performance, but of the extreme accuracy of the result there is no shadow of doubt.

We are indebted to A. Marshall, who has made use of Pickering's figures to calculate a formula and tables, which may be used for making up standard solutions of sulphuric acid with great accuracy and ease. Pickering's percentages are based upon the freezing points of concentrated sulphuric acid, and they are accurate within 0·01 per cent. As practically no volumetric method can be relied upon within less than 0·1 per cent. this leaves an ample margin Consideration of the figures shows that the strength of the acid can be determined with the necessary accuracy with least difficulty when the acid contains from 60 to 85 per cent. of H_2SO_4. Between these limits an error of 0·001 in the specific gravity or of 1° C. in the temperature will introduce an error of about 0·14 per cent. in the amount of acid, whereas outside the above limits the error introduced may be many times as great.

---

[1] *J. C. S. Trans.*, 1890, 64-184.

METHOD OF PROCEDURE: Highly pure sulphuric acid should be taken and diluted with water (preferably by adding the acid to the water). Cool the mixture to a convenient temperature and then determine its specific gravity. The temperature must be known within 0·5° C. and the specific gravity within 0·0005. If a Sprengel tube of 25 c.c. capacity be used, the weighings must be correct within 0·01 gram. The percentage of H_2SO_4 in the acid is then given by the formula:

$$P = D\,(85{\cdot}87 + 0{\cdot}05\,T - {\cdot}0004\,T^2) - 69{\cdot}80$$

where P = per cent. of H_2SO_4 in the acid
and D = density of the acid at T° C. referred to water at 4° C.

The above formula may be used for any temperatures from 0° to 40° C. and for acid containing 62 to 82 per cent. of H_2SO_4. The percentages given by it are correct within ± ·1 per cent.

The weight of acid required for the preparation of the standard solution can now be calculated.

Let A = grams of H_2SO_4 per litre in the required solution
and n = number of litres required
and W = weight of the acid which must be weighed out
Then

$$W = n\,A \times \frac{100}{P}$$

Weigh out W grams of the acid and make it up to n litres.

The percentages given by the above empirical formula are quite accurate enough for all ordinary purposes; the maximum error which could be introduced by employing them is about 1 in 1,500. More accurate values may, however, be obtained from Tables I. and II.; if great care be exercised, the error in the percentage need not then exceed 1 in 7,000. The weights, on which these tables were based, were fully corrected for air displacement. The weights of acid and water contained by the pyknometer, or Sprengel tube, must therefore be similarly corrected. Unless a very high degree of accuracy be aimed at, this correction may be made by subtracting 0·001 from the uncorrected specific gravity found.

The table at 18° C. (Table II.) is slightly more reliable than that at 15° C. (Table I.), as 18° was one of the temperatures at which Pickering actually determined the densities.[1]

Using these tables (p. 52) I have found that a normal acid of great accuracy may readily be prepared, and the strong solution may be kept intact in strength if placed in a well-stoppered bottle so as to preserve it from damp air. The fact that the concentrated acid is weighed, and not measured, is an additional security, and the weighing may take place within a large range of temperatures without any practical loss of accuracy.

As a check to the normal solution thus made I have used pure sodium carbonate prepared and weighed with the utmost care, and titrated by the help of methyl orange, with the most satisfactory results.[2]

4. Normal Oxalic Acid.

63·024 gm. $H_2C_2O_4,2H_2O$, or 45·01 gm. $H_2C_2O_4$ per litre.

This solution cannot very well be correctly prepared by direct weighing, owing to uncertain hydration of the crystallized acid; hence it must

---

[1] The figures given in these tables are only applicable to pure sulphuric acid.

[2] For valuable tables giving the relation of specific gravity to percentage for solutions of sulphuric, hydrochloric, and oxalic acids, see a paper by Worden and Motion, *J. S. C. I.*, 1905, **24**, 178.

Table I.

For ascertaining the Percentage Strength of Sulphuric Acid Solutions from the Specific Gravities at 15° C./15° C.

Specific Gravity	0.	1	2.	3.	4.	5.	6.	7.	8.	9.
1·60	68 72	68·80	68·89	68·97	69·06	69·15	69·23	69·32	69·40	69·49
1·61	69·58	69·66	69 75	69 84	69·92	70·01	70·09	70·18	70·26	70·35
1·62	70·43	70·52	70·60	70·69	70·77	70·86	70·94	71·03	71·11	71·20
1·63	71·28	71·37	71·45	71·54	71·62	71·71	71·80	71·88	71·97	72·05
1·64	72·13	72·22	72·30	72·39	72·47	72·56	72·64	72·73	72·81	72·90
1·65	72·98	73·07	73·15	73·24	73·32	73·41	73·49	73·57	73·66	73·74
1·66	73·83	73·91	74·00	74·08	74·17	74·25	74·34	74·42	74·51	74·59
1·67	74·68	74·76	74·85	74·93	75·02	75·10	75·19	75·27	75·36	75·44
1·68	75·52	75·61	75·69	75·78	75·86	75·95	76·03	76·12	76·21	76·29
1·69	76·38	76·47	76·55	76 64	76·72	76·81	76·90	76·98	77·07	77·15
1·70	77·24	77·33	77·41	77·50	77·59	77·67	77·76	77·84	77·93	78·02
1·71	78·10	78·19	78·28	78·36	78·45	78·53	78·62	78·71	78·79	78·88
1·72	78·97	79 05	79·14	79·22	79·31	79·40	79·48	79·57	79·65	79·74
1·73	79·83	79·91	80·00	80·09	80·18	80 27	80·37	80·46	80·55	80·64
1·74	80·73	80·82	80·91	81·00	81·10	81·19	81·28	81·37	81·46	81·55
1·75	81·64	81·73	81·83	81·98	82·01	82·11	82·21	82 30	82·40	82·50
1·76	82·60	82·70	82·79	82·89	82·99	83·09	83·19	83·28	83·38	83·48
1·77	83·58	83·68	83·77	83·87	83·97	84·07	84·16	84·26	84·36	84·15

Table II.

For ascertaining the Percentage Strength of Sulphuric Acid Solutions from the Specific Gravities at 18° C./18° C.

Specific Gravity.	0.	1.	2.	3.	4.	5.	6.	7.	8.	9.
1·60	68·89	68·97	69·06	69·15	69·23	69·32	69·40	69·49	69·58	69·66
1·61	69·75	69·83	69·92	70·01	70·09	70·18	70·26	70·35	70·43	70·52
1·62	70·61	70·69	70·78	70·86	70·95	71·03	71·12	71·20	71·29	71·37
1·63	71·46	71·55	71·63	71·72	71·80	71·89	71·97	72·06	72·14	72·23
1·64	72 31	72·40	72·48	72·57	72·65	72·74	72·82	72·91	72·99	73·08
1·65	73·16	73·25	73·33	73·42	73·50	73·59	73·67	73·76	73·84	73·93
1·66	74·01	74·10	74·18	74·27	74·35	74·44	74·52	74·61	74·69	74·78
1·67	74·86	74·95	75 03	75·12	75·20	75·29	75·37	75·46	75·54	75·63
1·68	75·71	75·80	75·88	75·97	76·05	76·14	76·22	76·31	76·40	76·48
1·69	76·57	76·65	76·74	76·82	76·91	76·99	77·08	77·17	77·25	77·34
1·70	77·42	77·51	77·59	77·68	77·77	77·85	77·94	78 03	78·11	78·20
1·71	78·29	78·37	78·46	78·55	78·63	78·72	78·81	78·90	78·98	79·07
1·72	79·16	79·24	79·33	79·42	79·51	79·59	79·68	79·77	79·85	79·94
1·73	80·03	80·12	80·21	80·30	80·39	80·48	80·57	80·66	80·75	80·84
1·74	80 93	81·02	81·12	81·21	81·30	81·40	81·49	81·58	81·67	81·76
1·75	81·86	81·95	82·04	82·14	82·24	82·34	82·44	82·53	82·63	82·72
1·76	82·82	82·92	83·02	83·13	83·23	83·32	83·42	83·52	83·62	83·72
1·77	83·82	84·92	84·02	84·12	84·22	84·33	84·43	84·54	84·65	84·77

be titrated by normal alkali of known accuracy, using phenolphthalein as indicator.

The solution is apt to deposit some of the acid at low temperatures, but keeps fairly well if preserved from direct sunlight, and will bear heating without volatilizing the acid. Very dilute solutions of oxalic acid are unstable; therefore, if a decinormal or centinormal solution is at any time required it should be made when wanted.

5. Normal Hydrochloric Acid.

36·468 gm. HCl per litre.

To prepare this, first of all distil a quantity of the ordinary pure concentrated acid (free from chlorine gas) from a capacious retort until one-third has passed over. The residual liquid[1] will contain 20·2 per cent. of hydrogen chloride, and 165 c.c. when diluted to one litre will form an almost exactly normal solution. Strong hydrochloric acid diluted to specific gravity 1020 is approximately normal. Or 120 gm., or 105 c.c. of the ordinary strong hydrochloric acid, which contains about one-third of its weight of the gas, may be diluted with water to one litre, which will then form a solution somewhat stronger than normal. This is now titrated with sodium carbonate exactly as described in section 3, p. 49, and diluted to exact strength.

Normal hydrochloric acid is most accurately standardized gravimetrically by precipitating the chlorine with excess of silver nitrate and weighing the silver chloride in a Gooch crucible. A simple and accurate process of standardization consists in immersing weighed pieces of Iceland spar in a measured volume of the acid, and noting the loss in weight of the spar after the acid is neutralized.[2]

Normal HCl has the advantages over normal H_2SO_4 that it gives with alkaline earths salts which are soluble both in water and in dilute alcohol, and that its strength can be controlled gravimetrically with silver nitrate. Hence, the general choice, at least for technical purposes, has fallen on hydrochloric acid as the standard acid. The sole disadvantage is that it volatilizes at a boiling heat.

G. T. Moody[3] describes a method of preparing an accurate standard acid which consists in passing gaseous HCl into water and weighing the amount absorbed. This requires a rather delicate arrangement of apparatus, but it is undoubtedly capable of great accuracy.

6. Normal Nitric Acid.

63·018 gm. HNO_3 per litre.

A rigidly exact normal acid should be prepared by means of sodium or calcium carbonate, as in the case of normal hydrochloric acid.

The nitric acid used should be colourless, free from chlorine and nitrous acid, specific gravity about 1·3. If coloured from the presence of lower oxides of nitrogen, it should be mixed with two volumes of water and boiled until colourless. When cold it may be diluted and titrated as previously described for sulphuric acid.

---

[1] Roscoe and Dittmar, *J. C. S.*, 1860, **12**, 128.

[2] Masson, *C. N.*, 1900, **81**, 73, and Green, *ibid.*, 1903, **87**, 5.

[3] *J. C. S. Trans.*, 1898, 658.

Also, 93 gm. or 65 c.c. of the ordinary strong nitric acid (sp. gr. 1·42) diluted to one litre gives a solution rather stronger than normal This is then titrated with sodium carbonate exactly as described in section 3, p. 49, and diluted to exact strength.

7. Normal Alkali Hydroxides (Caustic Soda or Potash).

40·008 gm. NaHO or 56·108 gm. KHO per litre.

Pure sodium hydroxide made from metallic sodium may now be readily obtained in commerce, and also powdered caustic soda of 98-99 per cent. purity, and a standard solution may be prepared from either of these. Weigh out rapidly about 42 gm.; dissolve in water, make up to a litre, and pour into the stock bottle. When quite cold fill a burette with the solution and titrate with 20 c.c. of normal sulphuric acid to which a drop or two of methyl orange has been added. The solution will be slightly strong and should be carefully adjusted by adding water till of correct strength. The final adjustment should be made by running it into 25 c.c. of normal acid. To make normal potassium hydroxide weigh out 58 gm. for a litre.

However pure caustic soda or potash may otherwise be, they are both in danger of absorbing carbonic acid, and hence in using litmus or phenolphthalein the titration must be conducted with boiling. Methyl orange permits the use of these solutions at ordinary temperature notwithstanding the presence of CO_2.

Sodium and potassium hydroxides may now both be obtained in commerce sufficiently pure for all ordinary titration purposes, and their solutions may be freed from traces of chlorine, sulphuric, silicic, and carbonic acids, by shaking with Millon's base, trimercur-ammonium.[1] Carbonic acid may also be removed by the cautious addition of barium hydrate in solution, shaking well, and then after settling ascertaining the exact strength of the clear liquid with correct standard acid.

In preparing these alkali solutions they should be exposed as little as possible to the air and, when the strength is finally determined, should be preserved in a bottle similar to that shown in fig. 12 or in full bottles having their glass stoppers slightly greased with vaseline.

8. Semi-normal Ammonia.

8·517 gm. NH_3 per litre.

This strength of standard ammonia is useful for saturation analyses in some cases; it is cleanly, does not readily absorb carbonic acid, holds its strength well when kept in a cool place and well stoppered, but is liable to develop flocculent growths. It may, however, be prepared in a few minutes by simply diluting strong liquid ammonia with freshly distilled water. An approximate solution may be made with about 28 c.c. of ·880 ammonia to the litre.

---

[1] *C. N.*, 42, 8.

A normal solution cannot be used with safety, owing to evaporation of the gas at ordinary temperatures.[1]

b. Decinormal Barium Hydroxide.

8·5693 gm. $Ba(OH)_2$ per litre.

This solution is best made from the crystallized hydroxide approximately of $^N/_{10}$ strength. This is done by shaking up in a stoppered bottle powdered crystals of barium hydroxide with distilled water, and allowing it to stand a day or two until quite clear. There should be an excess of the hydrate, in which case the clear solution, when poured off into a stock bottle fitted with a tube to prevent the entrance of CO_2 (see fig. 22 p. 23), will be nearly twice the required strength. It is better to dilute still further (after taking its approximate strength with $^N/_{10}$ HCl and phenolphthalein) with freshly boiled and cooled distilled water; the actual working strength may be checked by evaporating 20 or 25 c.c. to dryness with a slight excess of sulphuric acid, then igniting over a Bunsen flame and weighing the $BaSO_4$. The corresponding acid may be either $^N/_{10}$ oxalic, nitric, or hydrochloric, and the proper indicator is phenolphthalein. Oxalic acid is recommended by Pettenkofer for carbonic acid determination because it has no effect upon the barium carbonate suspended in weak solutions; but there is the serious drawback with oxalic acid that in dilute solution it is liable to lose its strength; therefore, if $^N/_{10}$ oxalic is used it should be freshly prepared from a normal solution.

The baryta solution is subject to constant change by absorption of carbonic acid, but this may be prevented to a great extent by preserving it in the bottle shown in fig. 22. A thin layer of light petroleum oil on the surface of the liquid preserves the baryta at one strength for a long period in the bottle shown in fig. 23.

The reaction between baryta and yellow turmeric paper is very delicate, so that the merest trace of baryta in excess gives a decided brown tinge to the edge of the spot made by a glass rod on the turmeric paper If the substance to be titrated is not too highly coloured, phenolphthalein should invariably be used.

Potassium tetroxalate, KHC_2O_4, $H_2C_2O_4$, $2H_2O$ (mol. wt. 254·156), is frequently used as a basis for alkalimetry, phenolphthalein (or litmus) being the indicator. For standardizing $^N/_{10}$ $Ba(OH)_2$ it is very useful, 0·25 gm. of the carefully prepared crystals, freed from moisture by pressing between blotting paper, requiring 29·51 c.c. of a barium hydroxide solution of strictly decinormal strength. Thus, the equation

$$2(KHC_2O_4,\ H_2C_2O_4,\ 2H_2O) + 3Ba(OH)_2 = K_2C_2O_4 + 3BaC_2O_4 + 10H_2O$$

shows that (254·156 × 2) = 508·312 gm. of the crystallized tetroxalate reacts with (171·386 × 3) = 514·158 gm. of $Ba(OH)_2$: or 0·25 gm. of the former would require $\frac{514 \cdot 158}{508 \cdot 312 \times 4} = 0 \cdot 25287$ gm. of the latter.

---

[1] Carulla (*J. S. C. I.*, 1907, **26**, 186) gives a series of experiments proving that N/2 ammonia retains its strength with great constancy under varying laboratory conditions.

And since 8·5693 gm. of BaH_2O_2 are present in 1000 c.c. of the decinormal solution, 0·25287 gm. corresponds to 29·51 c.c.

10. Normal Ammonium-Copper Solution for Acetic Acid and Free Acids and Bases in Earthy and Metallic Solutions.

This acidimetric solution is prepared by dissolving pure copper sulphate in warm water, and adding to the clear solution liquid ammonia until the bluish-green precipitate which first appears is nearly dissolved. The solution is then filtered into the graduated cylinder, and titrated by allowing it to flow from a pipette graduated in $\frac{1}{5}$ or $\frac{1}{10}$ c.c. into 10 or 20 c.c. of normal sulphuric or nitric acid (not oxalic). While the acid remains in excess, the bluish-green precipitate which is produced as each drop falls into the acid rapidly disappears; but so soon as the exact point of saturation is reached, the previously clear solution is rendered turbid by the precipitate remaining insoluble in the neutral liquid.

The process is especially serviceable for the determination of the free acid existing in certain metallic solutions, i.e. mother-liquors, etc., where the neutral compounds of such metals have an acid reaction on litmus—such as the oxides of zinc, copper, and magnesia, and the protoxides of iron, manganese, cobalt, and nickel; it is also applicable to acetic and the mineral acids.

If cupric nitrate be used for preparing the solution instead of sulphate, the presence of barium, or strontium, or metals precipitable by sulphuric acid is of no consequence. The solution is standardized by normal nitric or sulphuric acid; and as it slightly alters by keeping, a coefficient must be found from time to time by titrating with normal acid, by which to calculate the results systematically. Oxides or carbonates of magnesium, zinc, or other admissible metals, are dissolved in excess of normal nitric acid, and titrated residually with the copper solution.

Example: 1 gm. of pure zinc oxide was dissolved in 27 c.c. of normal acid, and 2·3 c.c. of normal copper solution required to produce the precipitate = 24·7 c.c. of acid; this multiplied by 0·0407, the coefficient for zinc oxide = 1·005 gm.

DETERMINATION OF THE ACTUAL STRENGTH OF STANDARD SOLUTIONS NOT STRICTLY NORMAL OR SYSTEMATIC.

In discussing the preparation of the foregoing standard solutions it has been assumed that they shall be strictly and absolutely correct; that is to say, if the same measure be filled first with any alkaline solution, then with an acid solution, and the two mixed together, a perfectly neutral solution shall result, so that a drop or two either way will upset the equilibrium.

Where it is possible to weigh directly a pure dry substance, this approximation may be very closely reached. Sodium carbonate, for instance, admits of being thus accurately weighed. On the other hand, the caustic alkalis cannot be so weighed, nor can the liquid acids. An approximate quantity, therefore, of these substances must be taken, and the exact strength of the solution found by experiment.

In titrating such solutions it is exceedingly difficult to make them so exact in strength that equal volumes, to a drop or two, shall neutralize each other. In technical matters a near approximation may be sufficient, but in scientific investigations it is of the greatest importance that the utmost accuracy should be obtained; it is therefore advisable to ascertain the actual strength, and to mark it upon the vessels in which the solutions are kept, so that a slight calculation will give the exact result.

Suppose, for instance, that a normal solution of sulphuric acid is being made and that on titration with a weighed amount of sodium carbonate it is found to be not of exact strength. Suppose, for example, that 1·9 gm. of sodium carbonate were dissolved in water and on titration required 36·1 c.c. of the solution instead of 35·85 c.c. of a solution of strictly normal strength. The solution used is obviously slightly weak, and of $\frac{35{\cdot}85}{36{\cdot}1} = 0{\cdot}993$ normal strength. Hence 0·993 is the factor by which it is necessary to multiply the number of c.c. of that particular acid in order to bring it to the normal strength.

In all circumstances it is safer to prove the strength of every standard solution by experiment, even though its active constituent has been accurately weighed in the dry and pure state.

Further, let us suppose that a solution of caustic soda is to be made from carbonate by means of fresh lime. After pouring off the clear liquid, water is added to the sediment to extract more alkali solution; by this means we may obtain two solutions, one of which is stronger than necessary, and the other weaker. Instead of mixing them in various proportions and repeatedly trying the strength, we may find, by two experiments and a calculation, the proportions of each necessary to give a normal solution, thus:—

The exact actual strength of each solution is first found by separately running into 10 c.c. of normal acid as much of each alkali solution as will exactly neutralize it. We have, then, in the case of the stronger solution, a number of c.c. required less than 10. Let us call this number V.

In the weaker solution the number of c.c. is greater than 10, represented by v. A volume of the stronger solution $= x$ will saturate 10 c.c. of normal acid as often as V is contained in x.

A volume of the weaker solution $= y$ will, in like manner, saturate $\frac{10y}{v}$ c.c. of normal acid; both together saturate $\frac{10x}{V} + \frac{10y}{v}$, and the volume of the saturated acid is precisely that of the two liquids, thus—

$$\frac{10x}{V} + \frac{10y}{v} = x + y.$$

Whence
$$10vx + 10Vy = Vvx + Vvy$$
$$vx(10 - V) = Vy(v - 10).$$

And lastly,
$$\frac{x}{y} = \frac{V(v + 10)}{v(10 - V))}$$

An example will render this clear. A solution of caustic soda was taken, of which 5·8 c.c. were required to saturate 10 c.c. of normal acid; of another solution, 12·7 c.c. were required. The volumes of each necessary to form a normal solution were found as follows:—

$$5{\cdot}8\,(12{\cdot}7 - 10) = 15{\cdot}66$$
$$12{\cdot}7\,(10 - 5{\cdot}8) = 53{\cdot}34$$

Therefore, if the solutions are mixed in the proportion of 15·66 c.c. of the stronger with 53·34 c.c. of the weaker, a correct solution ought to result. The same principle of adjustment is, of course, applicable to standard solutions of every class.

EXAMPLE: Suppose that 1 litre of normal soda were required. Since 15·66 + 53·34 = 69 it is clear that the fraction of the stronger solution to be taken is, in all cases,

$\frac{15{\cdot}66}{69}$ or $\frac{1566}{6900}$ or $\frac{522}{2300}$; and to get 1000 c.c. the volume required is

$$\frac{522 \times 1000}{2300} = \frac{5220}{23} = 227 \text{ c.c.,}$$

which has to be mixed with 1000 − 227 = 773 c.c. of the weaker solution.

Again: suppose that a standard solution of sulphuric acid has been made approximating as nearly as possible to the normal strength, and its exact value found by titration with sodium carbonate (or a standard hydrochloric acid with silver nitrate), and that such a solution has been calculated to require the coefficient 0·995 to convert it to normal strength. By the help of this solution, though not strictly normal, we may titrate an approximately normal alkali solution thus:—Two trials of the acid and alkaline solution show that 50 c.c. alkali = 48·5 c.c. acid having a coefficient of 0·995 = 48·25 c.c. normal; then, according to the equation, $50\,x = 48{\cdot}25$ is the required coefficient for the alkali, i.e.

$$x = \frac{48{\cdot}25}{50} = 0{\cdot}965.$$

And here, in the case of the alkali solution being sodium carbonate, we can bring it to exact normal strength by a calculation based on the equivalent weight of the salt, thus—

$$1 : 0{\cdot}965 :: 53 : 51{\cdot}145.$$

The difference between the two latter numbers is 1·855 gm., and this weight of pure sodium carbonate, added to one litre of the solution, will bring it to normal strength.

TABLE FOR THE SYSTEMATIC ANALYSIS OF ALKALIS, ALKALINE EARTHS AND ACIDS.

Substance.	Formula.	Molecular Weight.	Quantity to be weighed so that 1 c.c. Normal Solution = 1 per cent of substance.	Normal Factor.[1]
			grams.	
Sodium Oxide	Na_2O	62	3·1	0·031
Sodium Hydroxide	$NaOH$	40·008	4·0008	0·040008
Sodium Carbonate	Na_2CO_3	106	5·3	0·053
Sodium Bicarbonate	$NaHCO_3$	84·008	8·4008	0·084008
Potassium Oxide	K_2O	94·2	4·71	0·0471
Potassium Hydroxide	KOH	56·108	5·6108	0·056108
Potassium Carbonate	K_2CO_3	138·2	6·91	0·0691
Potassium Bicarbonate	$KHCO_3$	100·108	10·0108	0·100108
Ammonia	NH_3	17·034	1·7034	0·017034
Calcium Oxide (Lime)	CaO	56·07	2·8035	0·028035
Calcium Hydroxide	CaH_2O_2	74·086	3·7043	0·037043
Calcium Carbonate	$CaCO_3$	100·07	5·0035	0·050035
Barium Hydroxide	BaH_2O_2	171·386	8·5693	0·085693
Do. (cryst.)	$BaH_2O_2, 8H_2O$	315·511	15·7757	0·157757
Barium Carbonate	$BaCO_3$	197·37	9·8685	0·098685
Strontium Oxide	SrO	103·63	5·1815	0·051815
Strontium Carbonate	$SrCO_3$	147·63	7·3815	0·073815
Magnesium Oxide	MgO	40·32	2·016	0·02016
Magnesium Carbonate	$MgCO_3$	84·32	4·216	0·04216
Nitric Acid	HNO_3	63·018	6·3018	0·063018
Hydrochloric Acid	HCl	36·468	3·6468	0·036468
Sulphuric Acid	H_2SO_4	98·076	4·9038	0·049038
Oxalic Acid	$H_2C_2O_4, 2H_2O$	126·018	6·3024	0·063024
Acetic Acid	$C_2H_4O_2$	60·032	6·0032	0·060032
Tartaric Acid	$C_4H_6O_6$	150·048	7·5024	0·075024
Citric Acid	$C_6H_8O_7H_2O$	210·081	7·0027	0·070027
Carbonic Acid	CO_2	44	–	0·022
Arsenious Oxide	As_4O_6	395·84	4·948	0·04948

---

[1] This is the coefficient by which the number of c.c. of normal solution used in any analysis is to be multiplied in order to obtain the amount of pure substance present in the material examined.

THE TITRATION OF ALKALI SALTS.

1. Total Alkali in Caustic Soda or Potash, or Alkali Carbonates.

THE necessary quantity of substance being weighed or measured, as the case may be, and mixed with distilled water to a proper state of dilution (say about one per cent. of solid material), an appropriate indicator is added, and the solution is ready for the burette. Normal acid is then cautiously added till the change of colour occurs. In the case of caustic alkalis free from CO_2 the end-reaction is very sharp with any of the indicators; but if CO_2 is present, the only available indicators in the cold are methyl orange and lacmoid paper. If any other indicator is used, the CO_2 must be expelled by boiling after each addition of acid.

In examining carbonate of potash or soda, or mixtures of caustic and carbonate, where it is only necessary to ascertain the total alkalinity, the same method applies.

In the examination of samples of commercial refined soda or potash salts, it is advisable to proceed as follows:—

Powder and mix the sample thoroughly, weigh 10 gm. in a platinum or porcelain crucible, and ignite gently over a spirit or gas lamp, and allow the crucible to cool under the exsiccator. Weigh again, the loss of weight gives the moisture; wash the contents of the crucible into a beaker, dissolve and filter if necessary, and dilute to the exact measure of 500 c.c. with distilled water; after mixing thoroughly, take out 50 c.c. (= 1 gm.) of alkali with a pipette, transfer to a small flask, bring the flask under a burette containing normal acid and graduated to $\frac{1}{5}$ or $\frac{1}{10}$ c.c., and allow the acid to flow cautiously as before directed until the neutral point is reached. The process may then be repeated, in order to make certain of the correctness of the result.

Residual Titration. As the presence of carbonic acid with litmus and the other indicators, except methyl orange, always tends to make the exact end of the process doubtful, the difficulty is best overcome (when methyl orange is not used) by adding a known excess of acid to the alkali, boiling to expel the CO_2, cooling, and then cautiously adding normal caustic alkali, drop by drop, until the liquid suddenly changes colour; by deducting the quantity of caustic alkali from the quantity of acid originally used, the exact volume of acid necessary to saturate the 1 gm. of alkali is ascertained.

This method of residual titration gives a very sharp end-reaction, as there is no CO_2 present to interfere with the delicacy of the indicator. It is a procedure sometimes necessary in other cases, owing to the interference of impurities dissipated by boiling, e.g. H_2S, which would otherwise bleach the indicator,—except in the case of methyl orange or lacmoid paper, either of which is indifferent to H_2S in the cold. An example will make the procedure clear:—

Example: 50 c.c. of the solution of alkali prepared as directed, equal to 1 gm. of the sample, are run into a flask, and 20 c.c. of normal acid added; it is then boiled and shaken till all CO_2 is expelled, and normal caustic alkali added till the neutral point is reached; the quantity required is 3·4 c.c., which deducted from 20 c.c. of acid leaves 16·6 c.c. Supposing the alkali to be soda, the percentage present in the sample is arrived at thus: 1 c.c. $^N/_1$ acid = 0·031 gm. Na_2O, 16·6 × 0·031 = 0·5146 gm. Na_2O in 1 gm. of the sample, or 51·46 per cent. If carbonate is being determined, the amount would be 16·6 × 0·053 × 100 = 87·98 (say 88) per cent.

The following methods of ascertaining the proportions of mixed alkali hydroxides, monocarbonates, and bicarbonates must not be taken as absolutely correct, but are correct enough for technical purposes:—

2. Mixed Caustic and Carbonated Alkali Salts.

(*a*) **Precipitation of the Carbonate by Barium Chloride.**—The alkali salts of commerce often consist of a mixture of caustic and carbonated alkali. If it be desired to ascertain the proportions in these mixtures, the total alkalinity of a weighed or measured quantity of substance (not exceeding 1 or 2 gm.) is ascertained by normal acid and noted; a like quantity is then dissolved in about 150 c.c. of hot water in a 200 c.c. flask and only as much solution of barium chloride added as is sufficient to remove all CO_2 as exactly as possible, i.e., added until no further precipitate is produced. The following equation then represents the extent of the reaction:—

$$Na_2CO_3 + BaCl_2 = BaCO_3 + 2NaCl$$

and the titration of the supernatant liquid or the filtrate measures the alkalinity due to caustic alkali only.

If excess of barium chloride be added $Ba(OH)_2$ goes into solution in proportion equivalent to the caustic alkali, thus

$$2NaOH + BaCl_2 = Ba(OH)_2 + 2NaCl.$$

In this case, as Watson Smith[1] has shown, a low result in caustic alkali is obtained owing to the ready carbonation of the barium hydrate, which thus escapes titration.

The flask is now filled up to the 200 c.c. mark with distilled water, securely stoppered, and set aside to settle. When the supernatant liquid is clear, take out 50 c.c. with a pipette, and titrate slowly with normal hydrochloric acid. The number of c.c. used multiplied by 4 will be the quantity of acid required for the caustic alkali in the original weight of substance. The difference between the two titrations is calculated as carbonate. Or, the precipitated barium carbonate may be thrown upon a dry filter, washed well and quickly with boiling water, and titrated with normal acid, instead of the original determination of the total alkalinity, or both plans may be adopted so that one forms a check upon the other.

Sorensen and Anderson[2] have shown that this method only gives trustworthy results if the precipitation with barium chloride be carried out in the warmed solution, and when the latter contains only normal carbonates.

If the solution contains hydroxide or bicarbonate it must be treated with hydrochloric acid or sodium hydroxide before heating and precipitating. The quantity of acid or hydroxide required is ascertained by a previous determination. When a solution of pure normal carbonate is treated, while hot, with an excess of barium chloride, only normal barium carbonate is precipitated; if, however, the precipitation be performed at the ordinary temperature, more or less acid carbonate is thrown down, and the supernatant liquid becomes distinctly alkaline. Further, if the solution of the alkali carbonate contains hydroxide, a greater or less quantity of basic barium carbonate is precipitated on treating the hot solution with barium chloride.

---

[1] *J. S. C. I.*, 1, 85.

[2] *Z. a. C.*, 1908, 47, 279-294.

As barium hydroxide solution absorbs CO_2 very readily when exposed to the atmosphere, it is preferable to allow the precipitate of barium carbonate to settle in the flask as here described rather than to filter the solution, especially also as the filter obstinately retains some barium hydroxide.

A very slight error, however, occurs in this method in consequence of the volume of the precipitate being included in the liquid in the graduated flask. This error may be obviated by precipitating a small volume of the solution with barium chloride and titrating the liquid and precipitate in the same vessel with normal *oxalic acid* and phenolphthalein, this acid having no action on the barium carbonate.

(*b*) **Use of two Indicators.** On titrating the *cold* solution (as near 0° C. as possible) of mixed hydroxide and carbonate (to which 5 gm. of sodium chloride have been added per 50 c.c.) with normal acid and phenolphthalein, keeping tip of burette immersed in the liquid, the colour of the indicator is discharged as soon as all the hydroxide is neutralized and half the carbonate (by conversion into bicarbonate). On adding methyl orange (at most two drops) to the colourless solution and continuing the titration, the solution becomes pink as soon as the remaining half of the carbonate is neutralized. If the first addition of acid = **N** c.c., and the second **n** c.c., then **N** − **n** corresponds to hydroxide, 2 **n** to carbonate, and **N** + **n** to total alkali. In cases where **n** is greater than **N**, there can be no hydroxide present, only carbonate and bicarbonate, and the calculation is made as in 5 (*b*).

To ensure success in the determination it is necessary to prevent loss of CO_2. Hence a very dilute solution should be titrated, the acid should be run in from a burette having a long jet dipping into the liquid, and the latter should be contained in a narrow-mouthed vessel which is kept in gentle motion without causing air-bubbles, etc.[1]

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl.$$

The above method is sufficiently accurate for the determination of a small quantity of sodium carbonate in the presence of much sodium hydroxide, e.g. in caustic soda, but not of much carbonate with a small amount of hydroxide. The titration gives more correct results if sodium chloride is added, the introduction of ions of the same kind hindering the ionization of the sodium carbonate. A low temperature acts in the same direction.

3. Determination of Sodium or Potassium Hydroxide in presence of small proportions of Carbonate.

This may be accomplished by means of phenacetolin.[2] The alkaline solution is coloured a scarcely perceptible yellow with a few drops of the indicator. The standard acid is then run in until the yellow gives place to a pale rose tint; at this point all the caustic alkali is saturated, and the volume of acid used is noted. Further addition of acid now intensifies this red colour until the carbonate is decomposed; when a clear golden yellow solution results. The neutralization of the NaHO or the KHO is indicated by a rose tint permanent on standing; that of Na_2CO_3 or K_2CO_3 by the sudden passage from red to yellow.

---

[1] C. A. Seyler, *C. N.*, 1894, **70**, 187

[2] Lunge, *J. S. C. I.*, 1, 56.

Practice is required with solutions of known composition to accustom the eye to the changes of colour. Phenolphthalein may also be employed for the same purpose as follows:—

Add normal acid to the cold alkaline solution till the red colour is discharged, taking care to use a very dilute solution, and keeping the point of the burette in the liquid so that no CO_2 escapes. The colour is discharged when all the hydrate has been neutralized and the carbonate converted into bicarbonate; the volume of acid is noted, and the solution heated to boiling, with small additions of acid, till the red colour produced by the decomposition of the bicarbonate is finally destroyed.

In both these methods it is preferable, after the first stage, to add excess of acid, boil off the CO_2, and titrate back with normal alkali. The results are quite as accurate as the method of precipitation with barium.

4. Determination of small quantities of Sodium or Potassium Hydroxide in presence of Carbonates.

A method, by Thomson, consists in precipitating the carbonates by neutral solution of barium chloride in the cold: barium carbonate being neutral to phenolphthalein, this indicator can be used for the process. When the barium solution is added, a double decomposition takes place, resulting in the formation of an equivalent quantity of sodium or potassium chloride, while the barium carbonate is precipitated and the alkali hydrate remains in solution.

Example (Thomson). 2 gm. of pure sodium carbonate were mixed in solution with ·02 gm. of sodium hydroxide; excess of barium chloride was then added, together with the indicator, and the solution titrated with $^{N}/_{10}$ acid, of which in three trials an average of 5 c.c. was required; therefore, 5 × ·004 = ·02 gm.—exactly the quantity used.

In this process chlorides, sulphates, and sulphites do not interfere; neither do phosphates, as barium phosphate is neutral to the indicator. With sulphides, half of the base will be determined; but if hydrogen peroxide be added and the mixture allowed to rest for a time, the sulphides are oxidized to sulphates, which have no effect. If silicates or aluminates of alkali are present, the base will of course be recorded as hydroxide.

Thomson further states:—

"The foregoing method can also be applied to the determination of the hydrate of sodium or potassium in various other compounds, which give precipitates with barium chloride neutral to phenolphthalein, such as the normal sulphites and phosphates of the alkali metals. An illustration of the use to which the facts stated in this and former papers may be put will be found in the analysis of sodium sulphite. Of course sulphate, thiosulphate, and chloride are determined as usual, but to determine sulphite, carbonate and hydrate, or sodium bicarbonate, by methods in ordinary use is rather a tedious operation. To find the proportion of hydroxide, all that is necessary is to precipitate with barium chloride and titrate with standard acid, as above described. Then, by simple titration of another portion of the sample in the cold, using phenolphthalein as indicator, the hydroxide and half of the carbonate can be found, and, finally, by employment of methyl orange as indicator, and further addition of acid, the other half of the carbonate and half of the sulphite can be determined. By simple calculations, the respective proportions of these three compounds can be obtained, a result which can be accomplished in a few minutes. It must be borne in mind that if a large quantity of sodium carbonate is in the sample the proportion of that compound found will only be an approximation to the truth, as the end-reaction is only delicate with small proportions of sodium carbonate."

5. Determination of Alkali Carbonate and Bicarbonate in the presence of each other.

(*a*) The total alkali is first determined in one portion of the solution by titration with standard acid and methyl orange. To another portion a measured volume of standard sodium hydroxide (free from CO_2) is added, to convert the bicarbonate to carbonate. The sodium carbonate is then precipitated by barium chloride and the excess of hydroxide determined by titration with standard acid as in paragraph 2 (*a*). If **N** c.c. of normal acid correspond to the total alkali, **n** c.c. of normal sodium hydroxide be added, and **n′** c.c. normal acid correspond to the excess of the latter; then, **n** – **n′** c.c. = bicarbonate, and **N** – (**n** – **n′**) c.c. = carbonate. If **n** = **N**, thus ensuring excess of hydroxide, **n′** = carbonate.

(*b*) **Use of two Indicators.**—Titrating with acid and phenolphthalein to neutralization, then with acid and methyl orange, as in paragraph **2** (*b*), the first addition of acid (**n** c.c.) corresponds to half the carbonate, and the second addition (**N** c.c.) to half the carbonate + the total bicarbonate. Thus 2 **n** c.c. = carbonate, and **N** – **n** = bicarbonate.

This method of titration can be used for soda ash, etc., when carbonate and hydroxide or carbonate and bicarbonate occur in the same solution. [Cf. par. **2** (*b*).] Should the amount of $^N/_1$ acid used be greater with phenolphthalein than with methyl orange, NaOH is shown to be present, but if greater with methyl orange, then bicarbonate is present, and calculations for carbonate and hydrate, or carbonate and bicarbonate, are made in the usual way.

6. Determination of Alkalis in the presence of Sulphites.

It is not possible to determine the alkali compounds in the presence of sulphites by titration with acids, as a certain quantity of acid is taken up by the sulphite, SO_2 being evolved. This difficulty may be completely overcome by the aid of hydrogen peroxide, which speedily converts the sulphites into sulphates.[1] These operators proved that neither caustic nor carbonated alkali was affected by H_2O_2, nor had the latter any prejudicial effect on methyl orange in the cold. The quantity of H_2O_2 required in any given analysis must depend on the amount of sulphite present;

---

[1] Grant and Cohen, *J. S. C. I.*, 1890, **9**, 19.

for instance, the caustic salts of commerce contain about 50 per cent. of sulphite, and it suffices to take 10 c.c. of ordinary 10 vol. H_2O_2 for every 0·1 gm. of the salts in solution. In the case of mixtures containing less or more sulphite the quantity may be varied.

METHOD OF PROCEDURE: A measured volume of the peroxide is run into a beaker, and three or four drops of methyl orange added. As the H_2O_2 is invariably faintly acid, the acidity is carefully corrected by adding drop by drop from a pipette $^{N}/_{100}$ caustic soda. The required quantity of salt to be analysed is then added in solution, and the mixture gently boiled, whereby the methyl orange will be bleached. The liquid is then cooled, a drop or two more of methyl orange added, and the titration for the proportion of alkali carried out with normal acid. The results are very satisfactory.

7. Determination of Caustic Soda or Potash by standard Potassium Dichromate.

This process, or rather the inverse of it, was devised by Richter, for determining dichromate with caustic alkali by the aid of phenolphthalein. Exact results may be obtained by it in titrating soda or potash as hydrate, but not ammonia as recommended by Richter.

For the process there are required a decinormal solution of bicarbonate containing 14·72 gm per litre, and $^{N}/_{10}$ soda or potash solution titrated against sulphuric acid. A comparison liquid containing about 1 gm. of potassium chromate in 150-200 c c. water is advisable for ascertaining the exact end of the reaction; 50 c.c. of the alkali, having been diluted with the same volume of water, is coloured with phenolphthalein, and the dichromate run in from a burette; the fine red tint changes to reddish yellow, which remains till the neutral point is nearly reached, when the yellow colour of the chromate is produced. The change is not instantaneous, as with mineral acids, so that a little time must be allowed for the true colour to declare itself.

8. Direct Determination of Sodium by Potassium Dihydroxytartaric and Permanganate.

An interesting series of researches on the oxidation products of tartaric acid has been published by H. J. Horstman Fenton, M.A.[1] The results of these researches have been to develop the only method of obtaining sodium in such a form of combination as to admit of its volumetric determination. The author has kindly furnished me with specimens of dihydroxytartaric acid, and also of the potassium salt, with which to verify the results obtained by him, and I am able to state that when the method is carried out with extreme care and strict attention to details it is capable of giving satisfactory results.

Dihydroxytartaric acid, so far as present knowledge is concerned, is best prepared from dihydroxymaleic acid, and as both these acids are comparatively unknown their preparation will now be described.

---

[1] *J. C. S. Trans.*, 1894, pp. 899-910, 1898, pp. 71-81, *ibid*, 472-482, and on the volumetric determination of sodium, 1898, pp. 167-174.

Preparation of Dihydroxymaleic Acid.—Tartaric acid is dissolved in the least possible quantity of hot water; reduced iron (*ferrum redactum*) is added, and the liquid boiled until all the iron has disappeared. The quantity of iron must be insufficient to cause a separation of ferrous tartrate when the action is finished; about $\frac{1}{250}$ part of the weight of tartaric acid employed answers well, but the final result does not appear to be much influenced by the proportion of iron in solution, at any rate within considerable limits. The solution, filtered, if necessary, through cotton wool, is carefully cooled, surrounded by ice, and hydrogen peroxide (20 volume) added in small quantities at a time, allowing a few minutes to elapse between each addition. The first portions of the peroxide merely produce a yellowish colour, but, as the action proceeds, each addition produces a dark green or nearly black appearance, transient at first, but becoming more and more persistent. When this dark colour remains for two or three minutes, it is a rough indication that sufficient peroxide has been added. Great care must be taken not to add an excess of the peroxide, or the whole of the material will be wasted. Nordhausen sulphuric acid is now added by means of a thistle funnel, drawn out to a fine point, in very small quantities at a time, cooling carefully between each addition, preferably by ice and salt. The quantity added is a matter of importance, too much or too little giving an indifferent yield of the substance; the best proportion is found by experience to be about $\frac{1}{10}$th of the total volume of the liquid operated on. The mixture, still surrounded by ice, is put aside in a cold place, and after a few hours crystals begin to form. The first deposit is often discoloured and the crystals small, but the subsequent crops are beautifully white and pure. If the experiment is properly conducted, and the liquid kept sufficiently cool, crystals continue to form for several days, but the greater part are deposited within about 24 hours.

The crystals are collected with the aid of a pump, carefully drained, and washed repeatedly with small quantities of cold water. After again thoroughly draining, they are spread on filter-paper and air-dried. They appear to undergo no change in the air, even after several weeks' exposure

Preparation of Dihydroxytartaric Acid.—Crystallized dihydroxymaleic acid as above described ($C_4H_4O_6$, $2H_2O$) is well triturated with from 4 to 5 times its weight of glacial acetic acid, and rather more than the calculated quantity of bromine (1 mol acid to 1 mol. bromine) dissolved in a little glacial acetic acid, is added to the mixture in small portions at a time. The first portions are almost instantly bleached, but the action afterwards becomes more sluggish and apparently ceases. A few drops of water are then added, whereupon the colour of the bromine is again immediately discharged. The addition of bromine is continued until the colour is quite permanent on standing, even when a drop or two of water is added. This final stage is reached when the bromine has been added in about the calculated proportion; fumes of hydrogen bromide are freely evolved during the operation. The dihydroxymaleic acid is nearly insoluble in cold glacial acetic acid, but when the oxidation is finished complete solution takes place. The solution is allowed to stand for an hour or two and then vigorously stirred, when the dihydroxytartaric acid quickly, sometimes suddenly, separates as a heavy, white, cystalline powder.

The product is now collected and drained with the aid of a pump, washed once or twice with small quantities of anhydrous ether, and kept in a vacuum desiccator over solid potash and sulphuric acid to remove the last traces of hydrobromic and acetic acids, bromine and ether. The yield of purified product thus obtained is 70 per cent. or more of the theoretical. The formula for this acid is $C_4H_6O_4$.

The acid just described was first studied in relation to potassium permanganate by Fenton, and the reaction found to be quite definite; and bearing in mind the very sparingly soluble character of sodium dihydroxytartrate it appeared probable that a simple volumetric method for sodium might be devised. For complete precipitation it is necessary that the free acid shall be exactly neutralized, and this is most conveniently effected by first preparing the normal potassium salt. The employment of this salt as precipitant has also the advantage that risk is avoided of the precipitation of potassium with the sodium salt when the former metal is present in the mixture analysed.

Preparation of Potassium Dihydroxytartrate.—Weigh equivalent proportions of the acid 182, and dry potassium carbonate 138 parts. Dissolve separately in the least possible quantity of ice-cold water, then mix in a vessel surrounded by ice, and stir. Crystals soon separate, which may then be collected on a filter, and finally dried on changes of filter-paper in the air or in a desiccator. The salt so obtained does not, however, keep in proper condition for more than a few days, and therefore it is better to prepare it specially when sodium determinations have to be made. The formula of the salt is $K_2(C_4H_4O_8)H_2O$.

Standardizing the Permanganate Solution.—In this method of titrating soda it is preferable to standardize the permanganate upon pure sodium chloride rather than to depend on the relations between the acid and permanganate. The strength of the latter solution is best about $^N/_5$, i.e. 6·321 gm. of $KMnO_4$ to the litre. Its strength as regards the sodium to be determined is ascertained by the following procedure, bearing in mind that exactly the same process in every respect must be carried out in determining sodium in any given salt.

METHOD OF PROCEDURE.—About 0·2 gm. of pure sodium chloride is accurately weighed and dissolved in a small beaker with the least possible quantity of water, then placed in a basin and surrounded by ice. Then an excess, say 0·8 gm. of the potassium salt is weighed and dissolved in another small beaker, with not more than 25 c.c. of ice-cold water, placed in ice and stirred till dissolved; this occurs with some difficulty, but if the liquid is not free from floating particles or deposit, it must be quickly filtered into the sodium solution still standing in ice. The mixture is then allowed to stand in ice for half an hour with occasional stirring. The precipitated sodium salt is then collected by means of a small filter on filter plate and quickly drained with the water pump, then washed with 3 or 4 c.c. of ice-cold water three or four times in succession, and rinsing out the precipitating beaker. Finally, the precipitate is dissolved through the filter in a large excess of dilute H_2SO_4, rinsing out the precipitating beaker with dilute acid in the process, and titrated with the permanganate at ordinary temperature. The action on the permanganate is at first very slow, but when once commenced increases in force like the action of oxalic acid, and the end is quite distinct. The volume of permanganate having been noted, its working strength in relation to sodium in any available compound is ascertained, and marked on the bottle.

EXAMPLE.—0·21 gm. of pure NaCl was treated strictly according to the procedure just described, and required 48·3 c.c. of permanganate, not strictly $^N/_5$, but about that strength. The same weight of the same NaCl was then taken with about the same quantity of pure KCl in the same manner. The volume of permanganate used was 48·9 c.c. Taking into account the large volume of permanganate required for so small a quantity of sodium the difference was infinitesimal as regards the amount of sodium found. Practice undoubtedly renders the results more certain if exactly the same conditions are observed, more especially in keeping the temperature down to as near 0° as possible.

The process seems complicated, but when once the cooling arrangements are satisfactorily made it becomes very simple, and if there are a series of sodium determinations to be made, such as the alkali chlorides in mineral water residues, etc., it is far more rapid, and probably more exact, than the determination of the potassium by platinum, and calculating the sodium by difference.

It must be noted that the method is not available, so far as is known, in the presence of metals other than sodium, potassium, and magnesium. Ammonium should be removed, and borax cannot accurately be examined for its sodium. The metals should preferably be present as chlorides, sulphates, or nitrates; carbonates and hydroxides of sodium must be neutralized exactly with one of the mineral acids.

9. Determination of Potassium by means of Sodium Cobaltinitrite.

Sodium cobaltinitrite $[Na_3Co(NO_2)_6]$ under the name of de Koningh's reagent has long been known as a valuable qualitative test for potassium, with solutions of which it gives a canary-yellow precipitate. Its use for the quantitative determination of potassium, both gravimetrically and volumetrically, has been investigated by Adie[1] who, on adding a solution of sodium cobaltinitrite to a potassium salt, obtained a compound to which he gave the formula $K_2NaCo(NO_2)_6,H_2O$. The amount of K_2O in the precipitate may be found by means of a decinormal solution of permanganate. Cunningham and Perkin[2] have shown, however, that the precipitate may be a mixture of the tri- and di-potassium salts, $K_3Co(NO_2)_6$ and $K_2NaCo(NO_2)_6$, and emphasize the difficulty, also referred to by Adie, of washing the precipitate so as to obtain a clear filtrate. The constitution of the precipitate is shown to depend on whether the sodium cobaltinitrite or the potassium salt is in excess. Hence the authors consider that this method cannot be recommended for the analysis of potassium or cobalt compounds.

J. D. Jarrell,[3] after an examination of the method, found that it gave results about 2 per cent, too low as compared with those obtained by the platinum chloride method. The results of determinations on potassium chloride and on mixed fertilizers were very erratic; hence he considers the method in its present form unreliable.

Sodium cobaltinitrite is made as follows[4]:—

Dissolve 50 gm. of cobalt nitrate and 300 gm. of sodium nitrite in water, acidify by the addition of 25 c.c. of glacial acetic acid, and dilute to one litre. Allow to stand for 24 hours and filter. The solution is then ready for use.

10. Titration of Alkali Salts of Organic Acids.

The following salts of organic acids yield alkali carbonate on ignition. When the latter, in aqueous solution, is titrated with normal acid, the number of c.c. used multiplied by the factor tabulated below gives the weight of the corresponding salt.

---

[1] *J. C. S.*, 1900, **77**, 1076; see also W. A. Drushel; *Z. A. C.*, 1907, **56**, 223, 1908, **59**, 97; *Analyst*, 1908, **33**, 35 and 378

[2] *J. C. S.*, 1909, **95**, 1562.

[3] *Journal, A. O. A. C.* 1915, **1**, 29.

[4] A. H. Bennett—*Analyst*, 1916, **41**, 166.

Name of Salt.	Formula.	Normal Factor.	Logarithm.
Sodium acetate . . .	$NaC_2H_3O_2 . 3H_2O$	0·13607	$\bar{1}$·13377
,, benzoate . . .	$Na\ C_7H_5O_2$	0·14404	$\bar{1}$·15848
,, salicylate . . .	$Na\ C_7H_5O_3$	0·16004	$\bar{1}$·20423
Potassium acetate .	$K\ C_2\ H_3\ O_2$	0·09812	$\bar{2}$·99176
,, bitartrate .	$KHC_4H_4O_6$	0·18814	$\bar{1}$·27448
,, citrate . . .	$K_3C_6H_5O_7 . H_2O$	0·10812	$\bar{1}$·03391
,, tartrate . . .	$2K_2C_4H_4O_6 . H_2O$	0·11762	$\bar{1}$·07018
,, and sodium tartrate	$KNaC_4H_4O_6 . 4H_2O$	0·14110	$\bar{1}$·14953

TECHNICAL EXAMINATION OF SOME ALKALI COMPOUNDS FOUND IN COMMERCE OR PRODUCED IN COURSE OF MANUFACTURE.

There is now considerable unanimity among English and foreign manufacturers of alkali compounds as to methods of analysis to be adopted either for guidance in manufacture or for commercial valuation. Lunge[1] has contributed important papers on the subject, also in conjunction with Hurter in the *Alkali Makers' Handbook*[2] which contains valuable tables and processes of analysis. So far as volumetric methods are concerned, the same processes will be given here, together with others.

1. Soda Ash, Black Ash, Mother-liquors, etc.

Soda Ash or Refined Alkali.—5 or 10 gm. are dissolved in about 150 c.c. of warm distilled water, and any insoluble matter filtered off (German chemists do not filter), and the volume diluted to ½ or 1 litre.

The *total alkali* is determined in 50 c.c. by normal sulphuric, nitric, or hydrochloric acid, as on page 60, **1.**[3]

The *caustic alkali* present in any sample is determined as on page 61, **2.**

The presence of sulphide is ascertained by the smell of sulphuretted hydrogen when the alkali is saturated with an acid, or by dipping paper steeped in sodium nitro-prusside into the solution: if the paper turns blue or violet, sulphide is present.

The quantity of *sulphide and sulphite* may be determined by saturating a dilute solution of the alkali with a slight excess of acetic acid, adding starch, and titrating with $^{N}/_{10}$ iodine solution till the blue colour appears. The quantity of iodine required is the measure of the sulphuretted hydrogen and sulphurous acid present.

---

[1] *J. S. C. I.*, 1, 12, 16, 55, 92.

[2] This work now appears in an extended form under the title of *Technical Chemists' Handbook* (Gurney and Jackson, 1908).

[3] This gives a slight error, owing to traces of aluminate of soda and lime, which consume acid.

The proportion of *sulphide* is determined as follows: 13·820 gm. of pure silver are dissolved in nitric acid, 250 c.c. ammonia (·880) added, and the solution made up to a litre. Each c.c. = 0·005 gm. Na_2S.

METHOD OF PROCEDURE.—100 c.c. of the alkali liquor is heated to boiling, some ammonia added, and the silver solution dropped in from a burette until no further precipitate of Ag_2S is produced. Towards the end, filtration will be necessary in order to ascertain the exact point, to which end Beale's filter is serviceable. The amount of Na_2S so found is deducted from the total sulphide and sulphite found by iodine.

Sodium chloride (common salt) may be determined by carefully neutralizing 1 gm. of the alkali with nitric acid, and titrating with decinormal silver solution and potassium chromate. Each c.c. represents 0·005846 gm. of common salt. Since the quantity of acid necessary to neutralize the alkali has already been found, the proper measure of $^{N}/_{10}$ nitric acid may at once be added.

Sodium sulphate is determined either directly or indirectly, as under Sulphuric Acid. Each c.c. of normal barium chloride is equal to 0·071 gm. of dry sodium sulphate.

Black Ash.—Digest 50 gm. with warm water in a half-litre flask, fill up to mark, shake, and allow to stand till settled.

(1) *Total alkali* existing as carbonate, hydrate, and sulphide, is found by titrating 10 c.c. of the clear liquid (= 1 gm. of ash) with standard acid and methyl orange in the cold.

(2) *Caustic Soda.*—20 c.c. of the liquid are put into a 100 c.c. flask with 10 c.c. of solution of barium chloride of 10 per cent. strength, filled up with hot water, well shaken, and corked after settling a few minutes. The clarified liquid is filtered, and 50 c.c. (= 1 gm. ash), titrated with standard acid and methyl orange; or it may be titrated without filtration if standard oxalic acid and phenolphthalein are used, this acid having no effect on the barium carbonate. Each c.c. normal acid = 0·031 Na_2O. This includes sulphides.

3. *Sodium Sulphide.*—Put 10 c.c. of liquor into a flask, acidulate with acetic acid, dilute to about 200 c.c. and titrate with $^{N}/_{10}$ iodine and starch. Each c.c. = 0·0039 Na_2S, or 0·0031 Na_2O.

4. *Sodium Chloride.*—10 c.c. are neutralized exactly with normal nitric acid, and boiled till all H_2S is removed. Any sulphur which may have been precipitated is filtered off, and the filtrate titrated with $^{N}/_{10}$ silver and chromate. Each c.c. = 0·005846 gm. NaCl.

5. *Sodium Sulphate.*—This is best determined by precipitation as barium sulphate, and weighing, the quantity being small. If, however, volumetric determination is desired, it may be done as under Sulphuric Acid, taking 50 c.c. of liquor.

For other methods of examining the various solid and liquid alkali wastes used for soda and sulphur recovery, etc., the reader is referred to the *Technical Chemists' Handbook* already mentioned.

12. Salt Cake.

This is the somewhat impure sodium sulphate used in alkali manufacture or left in the retorts in preparing hydrochloric acid from sulphuric acid and salt.

Free acid is determined by dissolving 20 gm. of the sample, diluting to 250 c.c., taking out 50 c.c. (= 4 gm. salt cake) with a pipette, adding methyl orange, and titrating with standard sodium carbonate. The total acidity is calculated as SO_3, including HCl and $NaHSO_4$.

The *common salt* present is determined by decinormal silver solution and potassium chromate, having first saturated the free acid with pure sodium carbonate; 1 c.c. silver solution is equal to 0·005846 gm. of salt.

Sulphuric acid, combined with soda, is determined either directly or indirectly as under Sulphuric Acid; 1 c.c. of normal barium solution is equal to 0·071 gm. of dry sodium sulphate.

Iron is precipitated from a filtered solution of the salt cake with ammonia in excess, the precipitate of ferric hydrate re-dissolved in sulphuric acid, reduced to the ferrous state with zinc and titrated with permanganate.

13. Soap.

The following is a *résumé* of the methods given for the analysis of soaps by Lewkowitsch:—[1]

(1) *Water.*—This is usually found by difference. The sum of the percentages of fatty anhydrides and alkali in its various forms subtracted from 100 gives the water. For direct determination in exceptional cases about 5 gm.—carefully taken from the centre of a cake by cutting away all the outer portions—in thin shavings are put into a porcelain dish and weighed with a glass rod, which is used from time to time to break the skin that forms on drying and prevents the escape of water from the inner portions. Dry at 100° C. till of constant weight.

(2) *Fatty Matter and Total Alkali.* Weigh accurately 5-10 gm. of the sample and dissolve, with constant stirring, in hot water in a beaker or porcelain dish, heating gently. Add a few drops of methyl orange and acidify with a known volume of normal HCl or H_2SO_4. Heat with constant stirring until the separated fatty acids have melted into oily drops. Add a known weight (about 5 gm.) of dry beeswax or paraffin wax, and heat again until the mixture of fatty matter and wax appears as a clear, transparent layer on the surface of the liquid. Remove the stirrer, after rinsing with boiling water, heat till the fatty matter again collects into one mass, remove the vessel from the source of heat and set aside in a cool place. The solid cake that forms on the surface is then removed by means of a platinum spatula, rinsed with cold water and placed on filter paper. The sides of the vessel are carefully scraped and the scrapings added to the cake. The cake is dried by touching lightly with filter paper and placed bottom upwards on a watch glass, allowed to dry in a desiccator and weighed. The weight thus obtained, less the wax added, gives the *fatty matter*. If neutral fat, wax and unsaponifiable matter are absent, the result may be returned as *fatty acids* (rosin acids are regarded as so much fatty acids). In a complete analysis of a soap the fatty acids are multiplied by 0·9675 and the value so obtained returned as *fatty anhydrides*. The latter form a direct measure of the actual amount of soap present.

The acid liquid is filtered to remove traces of fatty acids and titrated back with $^{N}/_{2}$ soda or potash. The *total alkali* thus obtained is calculated to Na_2O in the case of hard soaps and to K_2O in the case of soft soaps.

---

[1] *Oils, Fats and Waxes*, 4th edition, vol. iii., p. 287, *et seq.*

(3) *Free caustic alkali.*—Dissolve a weighed portion of the soap 10-30 gm. in hot absolute alcohol and filter. The alkaline salts remain on the filter and the titration of the alcoholic filtrate with $^{N}/_{10}$ HCl, using phenolphthalein as indicator, gives the result required.

Should the alcoholic solution be acid, it must be titrated with $^{N}/_{10}$ alkali and the latter calculated to *free fatty acids*, expressed as oleic.

"Salting Out" Method.[1]—10 gm. are weighed into a 250 c.c. wide-necked flask, 50 c.c. of freshly boiled, hot distilled water added, the flask is lightly corked, and the whole heated on a hot plate until the soap is dissolved. 50 c.c. of a hot saturated solution of sodium sulphate is now added, the liquids thoroughly mixed by shaking, the contents of the flask transferred to a narrow-mouthed separating funnel, and the flask rinsed out into the separator with a further 5 c.c. of sodium sulphate solution. The separating funnel is then lightly corked, and stood perpendicularly in a beaker or other convenient stand in a hot-water oven. In a very short time the soap separates out on the surface, whilst the liquid beneath is an aqueous solution of sodium sulphate and any free alkali that was originally contained in the soap. This lower solution is run off into a beaker and titrated with $^{N}/_{10}$ sulphuric acid, using 5 per cent. silver nitrate solution as a spot indicator on a porcelain plate in the usual manner. If any appreciable amount of free hydroxide is found by this first titration, the separated soap in the separating funnel may be again washed with a further 50 c.c. of the sodium sulphate solution, and this when separated is titrated as before.

(4) The precipitate on the filter in (3) may contain carbonate, silicate, borate, etc. It is washed with cold water and the filtrate titrated with $^{N}/_{10}$ acid, using methyl orange as indicator. The number of c.c. used calculated as Na_2O give the alkali contained in the alkaline salts.

The sum of (3) and (4) subtracted from (2), gives the *combined alkali*.

Pure commercial soda soaps made by the hot process (termed "genuine soap") contain practically 30 per cent. of water and no more than 63-64 per cent. of fatty acids.

The theoretical composition of a genuine soap made from neutral glycerides having the mean molecular weight of about 860 (tallow, olive oil, etc.) is as follows:—

Fatty anhydrides	61·60	per cent.
Combined sodium oxide (Na_2O)	7·18	„
Water including small quantities of inorganic salts of glycerol (by difference)	31·22	„
	100·00	„

A genuine potash soap (soft soap) should theoretically have the following composition:—

---

[1] F. W. Newington, *J. S. C. I.*, 1916, **35**, 95.

Fatty anhydrides	38·70	per cent.
Combined potassium oxide (K_2O)	6·84	„
Glycerol, water, and potassium carbonate	54·46	„
	100·00	„

TITRATION OF ALKALI EARTHS AND THEIR COMPOUNDS.

STANDARD hydrochloric or nitric acid must in all cases be used for the titration of the caustic or carbonated alkali earths, as these are the only acids yielding soluble compounds, except in the case of magnesia. In titrating the oxides, such as caustic lime, baryta, strontia, or magnesia, any of the indicators may be used and the residual method should be adopted, viz., adding a known excess of standard acid, boiling to expel any trace of carbon dioxide, and then titrating the residual free acid by means of standard alkali.

The carbonates of the same bases may, of course, also be determined in the same way, bearing in mind that when methyl orange is used the liquid is best cooled before the final titration. All heating should be avoided when using methyl orange in titrating mixtures of oxide or hydroxides and carbonates, or the latter only, unless it is impossible to dissolve the substance in the cold. A good excess of acid is generally advisable.

The total amount of base in mixtures of caustic and carbonated alkaline earths is also determined in the same way.

(1) **Determination of Mixed Hydroxides and Carbonates.**—This may be done using either phenacetolin or phenolphthalein as indicator. The former has been recommended by Degener and Lunge; the method, however, requires practice in order to mark the exact change of colour.

METHOD OF PROCEDURE.—The liquid containing the compound in a fine state of division is tinted with phenacetolin so as to be of a faint yellow; normal acid is then cautiously added until a permanent pink occurs (at this stage all the hydroxide is saturated), more acid is now cautiously added until the colour becomes deep yellow—the volume of acid so used represents the carbonate.

The method is especially adapted to mixtures of calcium hydroxide and carbonate. It is also applicable to barium, but not to magnesium, owing to the great insolubility of magnesium hydroxide in dilute acid.

If phenolphthalein is used as indicator, the method is as follows:—

Heat the liquid to boiling, and cautiously add normal acid until the red colour is just discharged. The carbonates of calcium and barium, rendered dense by boiling, are both quite neutral to the indicator. To obtain the whole of the base, excess of normal acid is used, and the mixture titrated residually with normal alkali.

Magnesium in solution as bicarbonate may be accurately determined in the cold with methyl orange as indicator.

(2) **Determination of Calcium, Barium, Magnesium and Strontium in Neutral Soluble Salts.**—The amount of base in the chlorides and nitrates of the alkali earths may be readily determined as follows:—

The weighed salt is dissolved in water, cautiously neutralized if acid or alkaline, phenolphthalein added, the solution heated to boiling, and normal sodium carbonate delivered in from time to time with boiling until the red colour is permanent.

Magnesium salts cannot, however, be determined in this way, or even mixtures of lime and magnesia, as magnesium carbonate affects the indicator in a different manner from the other carbonates.

Nitrate of Lime (atmospheric). The nitrogen in this fertilizer may be indirectly determined by titrating the calcium present as nitrate with standard sodium carbonate.

The nitrate of lime must not contain the following:—(*a*) Nitrates of metals, the carbonates of which are soluble in water (alkali nitrates); (*b*) soluble oxides of metals, the carbonates of which are soluble in water (alkali oxides); (*c*) soluble salts of metals, the carbonates of which are insoluble in water, except nitrites and nitrates (e.g. $MgSO_4$, $CaCl_2$). I have found that these conditions are fulfilled by the leading brand of this fertilizer now on the English market, and this indirect method gives quite satisfactory results in comparison with the reduction and distillation process.

METHOD OF PROCEDURE: 10 gm. nitrate of lime [containing about 80 per cent. $Ca(NO_3)_2$] are dissolved in water and made up to 500 c.c. without filtration. 50 c.c. are transferred to a beaker or conical flask and 50 c.c. $^N/_5$ sodium carbonate added, boiled, and the precipitated calcium carbonate together with other insoluble substances, if present, filtered off. In the cooled filtrate the excess of sodium carbonate is titrated with $^N/_5$ hydrochloric acid and methyl orange. The Na_2CO_3 consumed corresponds to the $Ca(NO_3)_2$ present.

$$1 \text{ c.c. } ^N/_5\ Na_2CO_3 = \cdot0028 \text{ gm. N.}$$

Should the nitrate of lime contain free lime, this does not affect the titration, as an amount of sodium hydroxide is formed in the filtrate equivalent to the sodium carbonate consumed by the calcium hydroxide.

EXAMPLE: 50 c.c. of solution (= 1 gm. salt) + 50 c.c. $^N/_5$ Na_2CO_3 required 2·3 c.c. $^N/_5$ HCl. $50 - 2{\cdot}3 = 47{\cdot}7$ c.c. $^N/_5$ Na_2CO_3 consumed. $47{\cdot}7 \times {\cdot}0028 \times 100 = 13{\cdot}35$ per cent. nitrogen.

(3) **Precipitation of the Alkali Earths from their Neutral Salts as Carbonates.**—Soluble salts of calcium, barium, and strontium, such as chlorides, nitrates, etc., are dissolved in water, and the base precipitated as carbonate, with excess of ammonium carbonate and some free ammonia. The mixture is heated to about 60° C. for a few minutes. The precipitated carbonate is then to be filtered, well washed with hot water till all soluble matters, especially ammonia, are removed, and the precipitate with filter titrated with normal acid as already described.

Magnesium salts cannot be determined in this way.

(4) **Calcium and Magnesium Carbonates in Waters.**—The amount of calcium or calcium and magnesium carbonates dissolved in ordinary non-alkaline waters may be very readily, and with accuracy, found by taking 200 or 300 c.c. of the water, heating nearly to boiling, adding phenacetolin or lacmoid, and titrating cautiously with $^N/_{10}$ acid. An equally accurate result may be obtained by methyl orange in the cold liquid.

(5) **Determination of Calcium and Magnesium Sulphates, Chlorides, Nitrates, and Carbonates in Waters.**—See Water Analysis section.

AMMONIA.

$NH_3 = 17 \cdot 034$.

1. Determination of Combined Ammonia by Distillation with Alkalis or Alkali Earths.

This method brings about the expulsion of ammonia from all its salts. Caustic soda, potash, or lime may any of them be used. Where an organic nitrogenous compound exists in the substance it is in most cases necessary to submit it to preliminary treatment by Kjeldahl's method (p. 85).

There is a great variety of distilling vessels convenient for this process.

Any of the ordinary forms of apparatus will be found useful for accurately determining the ammonia in any of its compounds which can be decomposed by soda, potash, or lime. The gas so evolved is collected in a known volume in excess of standard acid, the excess of acid being afterwards found by residual titration with standard alkali. A compact modern form of apparatus is shown in fig. 26.

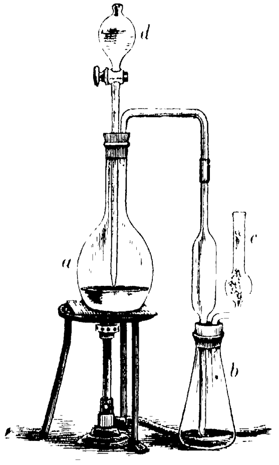

Fig. 26.

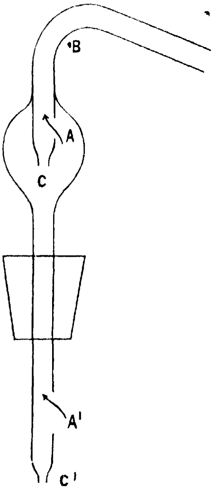

Fig. 27.

An ingenious and useful distillation tube for rapid determinations of ammonia designed by Hopkins[1] is shown in fig. 27. It is made from tubing of 7 to 8 mm. bore. The side openings, A and A_1, should be nearly as large, and the bulb about 5 cm. in diameter. The length of the tube below the bulb is 12 cm., and that above the bulb about the same. The jets C and C_1 are 2 mm. inside diameter. In use, the tube is pushed through the cork of the distilling flask until the opening A_1 is below the cork; the vapour then passes through the side openings, and whatever condenses in the tube below the bend B, runs back into the flask through the jets C and C_1, which always remain filled with liquid.

---

[1] *J. A. C. S.*, 1896, p. 227.

Method of Procedure.—The distilling flask *a* (see fig. 26), capacity about 400 c.c., is placed upon the wire gauze, and contains the ammoniacal substance. The tube *d* is filled with strong caustic potash or soda. The flask *b* holds about 300 c.c. and contains a measured quantity of standard acid, part being contained in the tube *c* which is filled with glass wool or broken glass, and through which the standard acid has been poured. The stoppers of the flasks should be of caoutchouc, failing which, good corks soaked in melted paraffin may be used.

The substance to be examined is weighed or measured, and put into the distilling flask *a* with a little water. The apparatus then being made tight at every point, some of the caustic alkali is allowed to flow into *a* by opening the tap of *d*, and the gas or spirit lamp is lighted under it.

The contents are brought to gentle boiling, taking care that the froth, if any, does not enter the distilling tube. It is as well to use a movable gas burner or common spirit lamp, so that, if there is any tendency to boil over, the heat can be removed immediately and the flask blown upon by the breath, which reduces the pressure in a moment. In examining guano and other substances containing ammoniacal salts and organic matter the tendency to frothing is considerable, and unless the above precautions are taken the accuracy of the results will be interfered with. A small piece of beeswax, solid paraffin, or granulated zinc is very serviceable in preventing frothing or bumping.

The distilling tube has both ends cut obliquely, and the lower end nearly, but not quite, reaches to the surface of the acid, to which a little methyl orange may be added. The quantity of standard acid used must, of course, be more than sufficient to combine with the ammonia produced; the excess is afterwards ascertained by titration with standard alkali. The boiling should be continued till about two-thirds of the liquor in the distilling flask have distilled over. The tube *c* must be thoroughly washed out into the flask *b* with distilled water, so as to carry down the acid with any combined gas which may have reached it. The titration then proceeds as usual. Each c.c. of $^N/_1$ acid neutralized by the ammonia = 0·017034 gm. of NH_3.

2. Indirect Method.

In the case of tolerably pure ammoniacal salts or liquids free from acid, or in which the free acid has previously been determined, a simple indirect method can be used, as follows:—

If the ammoniacal salt be boiled in an open vessel with normal caustic alkali the ammonia is entirely set free, leaving its acid combined with the fixed alkali. If, therefore, the quantity of alkaline solution is known, the excess beyond that necessary to replace the ammonia may be found by titration with normal acid. The boiling of the mixture must be continued till a piece of red litmus paper, held in the steam from the flask, is no longer turned blue.

Example: 5 gm. of a dirty sample of sulphate of ammonia were boiled on a sand-bath in a large flask with 100 c.c. of $^{N}/_{1}$ NaOH till all ammonia was expelled. On then titrating back with normal H_2SO_4 29·4 c.c. were required. The free acid in 5 gm. required 1·2 c.c. of $^{N}/_{1}$ NaHO. Hence 100 − 1·2 − 29·4 = 69·4, and ·017034 × 69·4 × 20 = 23·64 per cent. NH_3.

3. Technical Analysis of Ammoniacal Gas Liquor, Sulphate of Ammonia, Sal Ammoniac, etc. (arranged for the use of Manufacturers).

This process depends upon the fact that when ammoniacal salts are boiled with caustic soda, potash, or lime, the whole of the ammonia is expelled in a free state and may by a suitable apparatus (fig. 26) be determined with extreme accuracy (see p. 75).

Technical Analysis of Gas Liquor.—This liquid consists of a solution of carbonates, sulphates, thiosulphates, sulphides, thiocyanates (sulphocyanides), and other salts of ammonia. The object of the ammonia manufacturer is to get all these out of his liquor into the form of sulphate or chloride as economically as possible. The whole of the ammonia existing free or as carbonate in the liquor can be distilled off at a steam heat; the fixed salts, however, require to be heated with soda, potash, or lime (the latter is generally used on a large scale as being most economical, sometimes with an addition of caustic soda towards the end of the distillation), in order to liberate the ammonia contained in them.

The apparatus here described is the same on a small scale as is necessary in the actual manufacture of sulphate of ammonia in quantities; and its use enables any manufacturer to tell to a fraction how much sulphate of ammonia he ought to obtain from any given quantity of gas liquor. It also enables him to tell exactly how much ammonia can be distilled off with heat alone, and how much exists in a fixed condition requiring lime or caustic soda.

Strength of Ammoniacal Liquor.—Twaddell's hydrometer is always used for determining the density of ammoniacal liquor, the strength of which is approximately given in "oz. strength" by simply doubling the hydrometer reading. Thus, a liquor showing 5° Tw. might be roughly taken as of "10 oz. strength," which means that 10 ounces, by weight, of sulphuric acid (sp. gr. 1·842) are required to neutralize the ammonia present in one gallon of the liquor.

$$\text{oz. strength} = 4{\cdot}61 \times \text{gm. of } NH_3 \text{ per } 100 \text{ c.c.}$$

It should be noted that results should in all cases be given as "grams of ammonia per 100 c.c." not as "percentage of ammonia," because where a strong liquor of 15° or 17° Tw. is concerned, instead of ordinary gas liquor of about 5° Tw., it makes a considerable difference in a contract.

Solutions Required.

Standard Acid.—This is of such strength that each c.c. is equivalent to 0·1 gm. ammonia per 100 c.c. when 10 c.c. of the liquor are distilled.

Now a 1 per cent. ammoniacal solution contains 0·1 gm. NH_3 in 10 gm., and this requires 0·1 × 2·879 = 0·2879 gm. of H_2SO_4. This amount must be in 10 c.c. of the standard acid, since each c.c. of this = 0·1 gm. NH_3 per 100 c.c. of the liquor. Hence the standard acid must contain 28·79 gm. of H_2SO_4 per litre, and can be made by diluting 587·0 c.c. of $^N/_1$ H_2SO_4 to 1 litre.

Standard Soda.—This must exactly balance the standard acid and is made from normal soda solution in a similar way.

METHOD OF PROCEDURE.—Whatever the strength of the liquor, 10 c.c. is the amount invariably taken for distillation. This volume is pipetted into the distilling flask—the fittings having previously been removed—and the tube *d* (fig. 26, p. 75) is filled with strong caustic soda solution. The stopper is then replaced and the flask securely embedded in dry sand in a sand-bath or supported on wire gauze. 20-50 c.c. of standard acid (taking about 3 c.c. for each ounce of strength as determined above) are pipetted into the receiving flask through the tube *e*, which is filled with broken glass or glass beads placed on a layer of glass wool or fibrous asbestos. The acid thus retained serves to arrest any vapours of ammonia that may escape condensation in the flask. The apparatus is then fitted together, heat is applied to the sand-bath, and at the same time caustic soda solution is run into the flask by opening the tap on *d*. The contents of the flask are then heated to boiling point and the heating continued until the greater part of the liquid has distilled over into the receiver. The process usually takes about a quarter of an hour, and care must be taken that the tube in the receiver never dips into the acid distillate. The receiver with its attached tubes are then disconnected and the tube carefully washed down with distilled water till all traces of acid are brought into the flask. The fittings are now removed, the flask cooled, methyl orange or other suitable indicator added, and the residual acid titrated with the standard soda solution.

EXAMPLE: 10 c.c. of liquor of 5° Tw., equal approximately to 10 oz. strength, are distilled into 30 c.c. of the standard acid and 6 c.c. of standard soda are required to neutralize the excess. Then 30 − 6 = 24 c.c. of standard acid have been saturated by the distilled ammonia, equal to 2·4 gm. per 100 c.c., and 2·4 × 4·61 = 11·06 oz. strength.

METHOD OF PROCEDURE FOR SULPHATE OF AMMONIA OR SAL AMMONIAC. An average sample of the salt being drawn, 10 gm. are weighed, transferred to a 100 c.c. flask, distilled water poured on it, and well stirred till dissolved, and finally water added exactly to the mark. 10 c.c. of the well-mixed solution are pipetted into the distilling flask, 30 c.c. of standard acid are run into the receiving flask and the distillation carried on precisely as in the case of the gas liquor. The number of c.c. of standard acid required shows directly the percentage of ammonia; thus if 24·6 c.c. are used in the case of sulphate, it contains 24·6 per cent. of ammonia

The liquors when tested must be measured at ordinary temperatures, say as near 60° F. as possible. The standard solutions must be kept closely stoppered and in a cool place.

The following table is given to avoid calculations; of course, it will be understood that the figures given are on the assumption that the whole of the ammonia contained in the liquor is extracted in the manufacture as closely as it is in the experiment. With the most perfect arrangement of plant, however, this does not as a rule take place; but it ought to be very near the mark with proper apparatus, and care on the part of workmen.

Approximate measure of Standard Acid in c.c and tenths.	Percentage of Ammonia NH_3.	Ounce strength per gallon.	Weight of Sulphuric Acid in pounds and decimal parts required for each gallon of liquor			Yield of Sulphate per gallon in lb. and decimal parts.
			C. O. V. 169° Tw.	B. O. V. 114° Tw.	Chamber Acid 120° Tw.	
2·2	·2168	1	·0625	·0781	·0893	·0841
4·3	·4336	2	·1250	·1562	·1786	·1682
6·5	·6504	3	·1875	·2343	·2679	·2523
8·7	·8672	4	·2500	·3124	·3572	·3364
10·1	1·0840	5	·3125	·3905	·4465	·4205
13·0	1·3000	6	·3750	·4686	·5358	·5046
15·2	1·5176	7	·4375	·5467	·6251	·5887
17·3	1·7344	8	·5000	·6248	·7144	·6728
19·5	1·9512	9	·5625	·7029	·8037	·7569
21·7	2·1680	10	·6250	·7810	·8930	·8410
23·8	2·3840	11	·6875	·8591	·9823	·9251
26·0	2·6016	12	·7500	·9372	1·0716	1·0092
28·2	2·8184	13	·8125	1·0153	1·1609	1·0933
30·4	3·0350	14	·8750	1·0934	1·2502	1·1774
32·5	3·2520	15	·9375	1·1715	1·3395	1·2615
34·7	3·4688	16	1·0000	1·2496	1·4288	1·3456
36·9	3·6856	17	1·0625	1·3277	1·5181	1·4297
39·0	3·9024	18	1·1250	1·4058	1·6074	1·5138
41·2	4·1192	19	1·1875	1·4839	1·6967	1·5979
43·3	4·3360	20	1·2500	1·5620	1·7860	1·6820

The weight of sulphuric acid being given in decimals renders it very easy to arrive at the weight necessary for every thousand gallons of liquor, by simply moving the decimal point; thus 8-oz. liquor would require 500 lb. of concentrated oil of vitriol, 625 lb. of brown oil of vitriol, or 714½ lb. chamber acid for every 1000 gallons, and should yield in all cases 672·8 (say 673) lb. of sulphate.

4. Complete Technical Analysis of Ammoniacal Liquors.

The Annual Reports of the Chief Inspector under the Alkali, etc., Works Regulation Act have for some years past recorded the results of investigations conducted in his laboratory on ammoniacal liquors from various sources.

A general summary of the analytical methods in use was given in the Report for 1903 (pp. 31-39) and again in the Report for 1909 (pp. 15-19). From 1909-1917 no further investigations in this department were undertaken, but in the latter year liquors of exceptional strength were submitted for analysis and were found to require certain modifications of the methods ordinarily employed. In 1918 the procedure for determination of cyanogen compounds was submitted to further revision and the disturbing effect of thiocarbonate studied in detail, and suggestions made for its determination in liquors of varying strength (see Report 1918, Appendix; Report, 1919, Appendix). In Dec., 1919, the estimation of pyridine in sulphate of ammonia and in ammoniacal liquors was exhaustively reviewed (*ibid.*, 1919, Appendix). The general procedure for analysis of ammoniacal liquors is summarized in the Technical Index to the Alkali Reports with Appendix, 1894 to 1917, published in 1919.

The most recent processes will now be given, the special procedure required in the case of concentrated liquors[1] being distinguished by the letter (C).

Sampling.—Samples should be drawn from bulk and analysed fresh whenever practicable. If stored for subsequent analysis, care must be taken to exclude contact with air; glass stoppered bottles should be used, filled to within 2 c.c. of the stopper. Concentrated liquor should be handled with the greatest care. On storage thiocarbonate is converted into thiocyanate.

1. *Free Ammonia.*—(*a*) By direct titration, to determine approximately the volume of acid required for the distillation process. To avoid loss of ammonia by volatilization it is desirable to run the liquor into the standard acid, which is kept in excess until just before the end. Use methyl orange as indicator.

(*b*) By distillation. 10 c.c. of liquor (more, if weak) are diluted to about 350 c.c. in a round-bottomed flask connected through a catch bulb to Liebig condenser and receiver with inlet tube sealed in excess of $^{N}/_{2}$ H_2SO_4 and provided with outlet acid catch packed with fragments of hard glass (some beads are found to yield alkali to $^{N}/_{2}$ acid, and their use is not recommended). 200 c.c. of the solution are distilled over and the excess of acid in the receiver is titrated with $^{N}/_{2}$ Na_2CO_3. On further distillation certain liquors continue to evolve small traces of ammonia. The presence of this ammonia is attributed to the slow decomposition of fixed salts of ammonia and possibly of nitrogenous bodies, and the distillation for free ammonia is therefore not continued beyond 200 c.c.

2. *Fixed Ammonia.*—By distillation: Add 150 c.c of a 2 per cent. caustic soda solution to the residual liquor in flask used in (*b*) above and distil off 200 c.c. as before.

$$\text{c.c. } ^{N}/_{2} \text{ acid} \times 0{\cdot}0085 \times 10 = \text{gm. } NH_3 \text{ per 100 c.c.}$$

NOTE.—For method of stating results in terms of "Hydrogen Equivalents," see paper by L. T. Wright (*J. S. C. I.*, 1886, **5**, 655), also Appendix to Annual Report. 1905, p. 48.

3. *Carbonic Acid.*—10 c.c. of liquor (more, if weak) are diluted to 400 c.c. in a suitable flask provided with a Bunsen rubber valve; 10 c.c. of ammoniacal calcium chloride (1 c.c. = 0·44 gm. CO_2) are added and the whole heated for 2 hours in a water bath at 100° C. The calcium carbonate obtained by filtration is washed back into the flask with 25-30 c.c. of cold water, dissolved in $^{N}/_{2}$ HCl, and the excess of acid titrated with $^{N}/_{2}$ Na_2CO_3. The small amount of calcium carbonate left on the filter paper is best recovered by incineration and added to the contents of the flask.

$$\text{c.c. } ^{N}/_{2} \text{ acid} \times 0{\cdot}011 \times 10 = \text{gm. } CO_2 \text{ per 100 c.c.}$$

4. *Chloride.*—10 c.c of boiled liquor are diluted to 150 c.c., 25 c.c. of hydrogen peroxide (10 vols. "free from chloride") added, and the whole boiled for 15 minutes to oxidize thiocyanate, etc.: a further 10 c.c. of peroxide are then added and the

---

[1] The manufacture and analysis of commercial concentrated ammonia liquor is dealt with by Colman and Yeoman, *J. S. C. I.*, 1918, **37**, 319 T.

boiling continued for 5 minutes. To the hot solution are added five or six drops of a 10 per cent. solution of potassium chromate and the boiling continued for two minutes, then a few drops of sodium carbonate with further boiling for one minute. The solution, which should possess a yellow colour, is filtered, cooled, and made up to 250 c.c.; an aliquot portion is then titrated with $^{N}/_{10}$ $AgNO_3$ (potassium chromate indicator) after neutralizing with dilute nitric acid. A blank experiment is made with 10 c.c. of $^{N}/_{10}$ NaCl and the same volumes of water, peroxide, and chromate as in the actual analysis, to determine the correction for traces of chloride in the reagents used.

It is desirable, after oxidation with the peroxide and before addition of the chromate, to test a drop of the solution with iron alum acidified with nitric acid to ensure that all the thiocyanate has been oxidized. Should oxidation be incomplete or the organic matter in solution resist oxidation, further additions of peroxide and potassium chromate must be made and the boiling continued as before.

c.c. $^{N}/_{10}$ $AgNO_3 \times 0{\cdot}00364 \times 10$ = gm. HCl per 100 c.c.

NOTE.—If more than a trace of ferrocyanide is present in the sample, it is removed by addition of iron alum prior to oxidation with peroxide. Thus:

10 c.c. of the boiled liquor are diluted to 100 c.c. and heated to 60°-70°. A sufficient excess of a saturated solution of iron alum is then added. After coagulation the Prussian blue is removed by filtration and washed with water containing a little sodium sulphate. The filtrate is then oxidized with peroxide as described above.

5. *Sulphur.*—(*a*) As sulphate (by Dyson's method). 250 c.c. of the liquor are concentrated to about 10 c.c. on the water bath, 2 c.c. of strong hydrochloric acid added, and the evaporation continued to dryness to decompose thiosulphate and render organic matter less soluble. The residue is extracted with water, and the filtered solution made up to 250 c.c., 100 c.c. of this solution are acidified with hydrochloric acid, brought to the boil, and barium chloride added; the precipitate, after standing, is filtered and weighed.

During evaporation the liquor should be protected from contact with products from the combustion of coal gas, as sulphureous fumes are readily absorbed.

gm. $BaSO_4 \times 0{\cdot}1373$ = gm. sulphur, as sulphate, per 100 c.c.

(*b*) As (i) sulphide; (ii) sulphite and thiosulphate.

Approximate method: 10 c.c. of the liquor are run into 400 c.c. of water acidified with hydrochloric acid and containing a moderate excess of $^{N}/_{10}$ iodine solution. The excess of iodine is then titrated with $^{N}/_{10}$ thiosulphate, starch indicator.

Exact method. 10 c.c. of liquor (or more) are run into excess of $^{N}/_{5}$ ammoniacal zinc chloride solution diluted to about 80 c.c.; the solution is warmed to coagulate the sulphide, filtered, and the precipitate washed with warm water.

(i) Sulphide.—The zinc sulphide on the filter is washed into excess of $^{N}/_{10}$ iodine strongly acidified with hydrochloric acid (the last traces of sulphide being washed through with cold dilute acid, or the filter paper may be digested with dilute acid and a little iodine). After vigorous shaking to complete the solution of the sulphide (and on occasions solution is slow), the excess of iodine is determined with $^{N}/_{10}$ thiosulphate, starch indicator.

c.c. $^{N}/_{10}$ iodine $\times 0{\cdot}0016 \times 10$ = gm. sulphur, as sulphide, per 100 c.c.
" " $\times 0{\cdot}0017 \times 10$ = gm. sulphuretted hydrogen per 100 c.c.

(*c*) In the analysis of concentrated liquor 10 c.c. are run into excess of ammoniacal zinc chloride, hydrochloric acid equivalent to the liquor taken is then cautiously added, with agitation to avoid local excess, the alkaline solution filtered, and the residue well washed with warm water. The sulphide in the residue and the thiosulphate in the filtrate are then determined by titration with $^N/_{10}$ iodine.

(ii) Sulphite and Thiosulphate.—An approximate method for the differentiation of sulphite and thiosulphate was described in Annual Report, 1903, p. 36. Mayer and Hempel[1] describe a method based upon the use of strontium chloride, which they consider to be sufficiently accurate for the desired purpose. Prolonged experience in the analysis of ammoniacal liquors, however, has led the author to the conclusion that no exact estimation of sulphite and thiosulphate is possible in such liquors by any method based on titration with iodine, save in quite exceptional cases, and he prefers to present a *united* figure for sulphur as sulphite, thiosulphate and other forms reached by "difference": by subtracting from the "total sulphur" found by bromine oxidation the sulphur present in the form of sulphate, thiocyanate, and sulphide separately determined.

(c) *Sulphur as Thiocyanate* (Sulphocyanide).—250 c.c. are run into a graduated flask provided with a rubber stopper fitted with inlet small bore tube and pinchcock and connected to a supply of coal-gas. 10 gm. of lead carbonate are added, and the air in the neck of the flask displaced by coal-gas. The stopper is then pushed in, the pinchcock closed, and the flask well shaken until the sulphide separates, leaving the supernatant liquor clear and colourless. In certain cases further addition of lead carbonate is found necessary, and in any case it is desirable to test a drop of the supernatant liquor with lead acetate paper before proceeding with the analysis, as follows:—

150 c.c. of the clear supernatant liquor are withdrawn and boiled for 10 to 15 minutes to remove the cyanide, and the solution cooled and made up to 150 c.c.

50 c.c. of this solution (= 50 c.c. of the original liquor) are slightly acidified with sulphuric acid and the ferrocyanide removed as Prussian[2] blue by the cautious addition of a solution of iron alum in slight excess, followed by filtration through paper pulp with the aid of the filter pump. The residue is well washed with hot water containing a little sodium sulphate, to prevent "re-solution" of the blue, and the thiocyanate in the filtrate determined in one of the two following ways:—

(i) *Direct Titration, after Oxidation of the Thiosulphate by Iron Alum.*—To the filtrate (cold) add 1 c.c of a saturated solution of iron alum and heat the mixture to incipient boiling. To the hot solution add 1 c.c. more of the iron solution and allow the mixture to stand 5 minutes to complete the oxidation and promote separation of ferric hydrate. The blood-red solution is then filtered through paper pulp, the residue washed with hot water and the filtrate (which should be bright and clear or brown end-point will follow) is cooled, acidified with 2 c.c. of 50 per cent. nitric acid (free from chloride and from oxides of nitrogen) and titrated with $^N/_{10}$ $AgNO_3$ in the usual way. A more certain end-point is reached if a slight excess of silver solution is added, say, 0·5 c.c. and the liquor filtered and brought back with $^N/_{10}$ AmSCy. Results are slightly high.

(ii) *Precipitation as Cuprous Thiocyanate.*—To the blood-red filtrate from the Prussian blue a distinct excess of a solution of sodium metabisulphite is added—say, 10 drops in all of a concentrated solution—and the mixture heated to 60°-70° C to effect reduction of the ferric salt. A distinct excess of a 10 per cent. solution of copper sulphate is then added and the heating continued to incipient boiling. After standing 5 to 10 minutes with occasional agitation to effect coagulation of the cuprous thiocyanate and associated impurities, the solution is filtered and the precipitate well washed with hot water until the washings remain colourless on addition of a drop of dilute solution of ferrocyanide. The filter paper is then pierced, the residue washed back into the flask and 25 c.c. of a 4 per cent. solution of NaOH (free from chloride) run into the flask over the filter paper, and the contents digested for 5 to 10 minutes (at about 40° C.) to complete the decomposition of the cuprous salt. The solution is then filtered through paper pulp, the residue well washed with hot water, and the filtrate cooled, acidified with 5 c.c. of 50 per cent. nitric acid and titrated with $^{N}/_{10}$ $AgNO_3$, after addition of a little iron alum as indicator. It is advisable to add excess of the silver solution and to titrate back, after filtration, as in (i) above.

---

[1] *J. für Gasbeleucht.* 1908.

[2] Ammonium ferrocyanide is somewhat unstable on boiling, but in absence of ammonium sulphide there will be no formation of thiocyanate The Prussian blue obtained is rejected.

Dr. Colman finds it an advantage, in certain cases, to add a few drops of iron alum to the caustic soda extract of the cuprous salt before filtration to promote coagulation.

If the amount of thiocyanate is small—say, less than the equivalent of 5 c.c. $^{N}/_{10}$ $AgNO_3$ in the volume taken for precipitation—it is found an advantage to add to the filtrate from the Prussian blue, and prior to precipitation with copper sulphate, 10 c.c. of $^{N}/_{10}$ NH_4SCy. Allowance is made in the titration for this addition, and 0·15 c.c $^{N}/_{10}$ $AgNO_3$ is added to the titre to correct for the solubility of the cuprous thiocyanate and other losses incidental to the process, as determined by blank experiment.

c.c. $^{N}/_{10}$ $AgNO_3 \times 2 \times \cdot 0032$ = gm. sulphur, as thiocyanate, per 100 c.c.
$\times 2 \times \cdot 0027$ = gm. HCN, as thiocyanate, per 100 c.c.

(*d*) *Total Sulphur* (Dyson's method modified).—50 c.c. of the liquor (100 c.c. if weak) are slowly added drop by drop, and with constant shaking, to 50 c.c. of water containing excess of bromine (free from sulphur) acidified with a moderate excess of hydrochloric acid. The oxidized solution is evaporated to dryness on the water-bath (avoiding contact with acid fumes from coal gas), the residue extracted with boiling water, filtered, cooled, made up to 250 c.c. and 100 c.c., precipitated with barium chloride solution in the usual way.

$$\text{gm. } BaSO_4 \times \cdot 1373 \times 5 = \text{gm. sulphur in 100 c.c.}$$

In the case of certain liquors, e.g. coke and blast-furnace liquors, oxidation with bromine yields a heavy yellow precipitate of brominated phenols. This precipitate may retain traces of sulphate in amount sufficient to affect the percentage distribution figure, unless it is recovered by fusion with the smallest quantity of potassium carbonate and nitrate, or sodium peroxide, and included in the total.

6. *Ferrocyanide* (Feld's method modified).—Dr. Colman has emphasized the importance of safeguarding the stability of the ferrocyanide when effecting the removal of the cyanide and sulphide prior to precipitation of the ferrocyanide as Prussian blue. The ammonium salt suffers partial decomposition at boiling temperature, and some loss of cyanogen is noticeable even where the solution is boiled at 40° under reduced pressure. On the other hand, solutions of sodium and potassium ferrocyanide are stable at the boiling temperature, even in presence of ammonia, if sufficient caustic alkali is present.

Mayer and Hempel take 250 c.c. of liquor, acidify slightly with sulphuric acid, and add iron alum solution in sufficient excess to impart a deep red coloration (ferric thiocyanate). The solution is then heated to 60° C. and the Prussian blue separated by filtration. Should the filtrate be coloured blue, it must be returned to the filter and the process repeated until a small quantity shows no blue colour after addition of mercuric chloride to destroy the ferric thiocyanate. The precipitate is then washed two or three times with water containing sodium sulphate. Filter and precipitate are next transferred to a flask and the Prussian blue decomposed by boiling for 5 minutes with 10 c.c. of normal caustic soda, and the solution diluted to 150 c.c.; 15 c.c. of magnesium chloride solution (610 gm. $MgCl_2\,6H_2O$ per litre) are next added to the boiling solution very slowly and with constant agitation to avoid the formation of clots of magnesium hydroxide. To the boiling mixture about 100 c.c. of boiling mercuric chloride solution (27·1 gm. $HgCl_2$ per litre) are added, and the whole is boiled for 5 to 15 minutes. The liquor is then distilled for 20 to 30 minutes with addition of 30 c.c. of 4N sulphuric acid (196 gm. H_2SO_4 per litre), the hydrocyanic acid being collected in 25 c.c. of normal caustic soda and titrated as described in the method for estimation of hydrocyanic acid below.

$$\begin{aligned} 1 \text{ c.c. } {}^{N}/_{10}\ AgNO_3 &= 0{\cdot}0051 \text{ gm. } HCy \\ &\ 0{\cdot}00947 \text{ gm. } (NH_4)_4FeCy_6. \end{aligned}$$

For H. E. Williams's method of procedure for determination of ferrocyanides, see Part V, Ferrocyanides.

7. *Hydrocyanic Acid*, by Feld's method.—If caustic ammonia is absent 50 c.c. of the liquor are distilled with excess of a strong solution of lead nitrate.

The apparatus employed is similar to that used for estimation of ammonia and ferrocyanide. It consists of a 500 c.c. round-bottomed flask provided with two-holed caoutchouc stopper with inlet tube sealed in liquor and exit tube connected through a catch bulb to Liebig condenser and receiver. The exit tube of the condenser is sealed in the 25 c.c. of normal soda with which the receiver is charged, residual gases escaping through a scrubbing bulb containing fragments of hard glass moistened with caustic soda. The distillate is diluted to 400 c.c., a crystal of potassium iodide added, and the solution titrated on ${}^{N}/_{10}$ $AgNO_3$.

$$\text{c.c. } {}^{N}/_{10}\ AgNO_3 \times {\cdot}0051 \times 2 = \text{gm. } HCy \text{ per } 100 \text{ c.c.}$$

If caustic ammonia is present, results are low in presence of thiosulphate,[1] and the following procedure is adopted in the case of ordinary liquors. 150 c.c. of the liquor are shaken with lead carbonate (to remove sulphide) in presence of coal-gas in the manner described in 5(*c*) above.

50 c.c. of the clear supernatant liquor are run into a slight excess of a 25 per cent. solution of aluminium chloride diluted to 200 c.c. The solution should then be acid to litmus paper. Normal sodium carbonate solution is then added in amount sufficient to render the solution distinctly alkaline to litmus, followed by addition of 10 c.c. of a 20 per cent. solution of lead nitrate, which should render the mixture acid to litmus. The hydrocyanic acid is then obtained by distillation as described above.

Certain ammoniacal liquors, e.g. coke-oven liquors, froth considerably on distillation with lead nitrate. The flask should therefore be heated cautiously. In general, the distillation will be complete when 100 c.c. of water have passed over, say, 20 to 25 minutes' gentle boiling.

(C) The method is also applicable for determination of cyanide in concentrated liquor: 50 c.c. of the clear supernatant liquor, freed from sulphide as described above, are diluted and boiled to remove the bulk of the ammonia, after addition of 25 c.c. of normal caustic soda to fix the cyanide. The cooled liquor is then run into excess of aluminium chloride solution, and the cyanide recovered by distillation as described above.

8. *Phenols.*—These may be determined by the method described by Dr. F. W. Skirrow (see *J. S. C. I.*, 1908, **27**, 58).

9. *Pyridine.*—Dr. Colman employs the method of Pennock and Morton (*J. Amer. C. S.*, 1902, **24**, 377), an account of which is given in Lunge and Keane's *Technical Methods of Chemical Analysis*, II, ii, 743. See also Alkali

---

[1] Due to the fact that if caustic ammonia (or caustic alkali) and thiosulphate are both present in the solution, sulphur results from decomposition of lead thiosulphate on boiling and this sulphur in presence of lead oxide (or ammonia) and cyanide yields non-volatile thiocyanate.

Report, 1919, Appendix, for critical review of this and other methods for determination of pyridine.

The following factors will be found useful to convert :—

CO_2	into	$(NH_4)_2CO_3$	multiply	by 2·181
$(NH_4)_2CO_3$	,,	$2NH_3$	,,	,, 0·355
HCl	,,	NH_4Cl	,,	,, 1·467
NH_4Cl	,,	NH_3	,,	,, 0·318
$2NH_3$	,,	$(NH_4)_2SO_4$	,,	,, 3·88
H_2SO_4	,,	$(NH_4)_2SO_4$	,,	,, 1·317
HCy	,,	NH_4Cy	,,	,, 1·630
6HCy	,,	$(NH_4)_4FeCy_6$	,,	,, 1·752
HCy	,,	NH_4SCy	,,	,, 2·817
S	,,	$(NH_4)_2SO_4$	,,	,, 4·122
S_2	,,	$(NH_4)_2S_2O_3$	,,	,, 2·311
H_2S	,,	$(NH_4)_2S$	,,	,, 2

EXAMPLE A sample gave 2 grams CO_2 per 100 c.c. This equals 2·184 × 2 = 4·368 grams $(NH_4)_2CO_3$.

5. The Determination of Nitrogen in Organic Bodies.

The well-known method of Varrentrapp and Will for the determination of nitrogen, other than nitric nitrogen, in organic bodies by combustion with soda-lime and absorption of the gaseous ammonia so produced in a measured volume of standard acid, the excess of which was determined by titration with standard alkali, has long been abandoned in favour of the Kjeldahl process (see below). The process of Ruffle, by which nitrogen could be determined in substances containing some of their nitrogen in the form of nitrate, has likewise been entirely superseded by the Jodlbauer modification of the Kjeldahl method. Hence, no further reference need be made to either of these methods, though each of them gave good results and was largely used in its day. As a means of control over all other methods of nitrogen determination that of Dumas, commonly known as the "absolute method," may be used. In this method the substance is heated with copper oxide in a tube so arranged that the products of the oxidation pass over red-hot copper oxide and metallic copper. The gaseous products of the combustion are freed from carbon dioxide by passing through caustic potash solution and the whole of the nitrogen present in whatever form will be obtained in a free state and can be measured. Full working details of this process will be found in standard works on organic chemistry.

6. Kjeldahl's Method, and its Developments.

In this process, which was introduced in 1883,[1] ammonium sulphate is produced by moist combustion of the nitrogenous substance with sulphuric acid, and the salt thus formed is subsequently distilled with excess of caustic alkali. The free ammonia so produced is absorbed by a known volume of a standard acid solution, present in excess, the residual amount being determined by titration. The method as originally introduced, was applicable only to nitrogenous organic compounds in the absence of nitrates, but by various modifications it has now been made applicable to all cases, with the possible exception of a few alkaloidal and allied bodies. One of the many advantages of the method is that the nitrogenous substance need not be reduced to a finer state of division than is necessary to secure a fair sample. The theory of the reactions whereby the final product of heating a nitrogenous organic compound with sulphuric acid and an oxidizing body is ammonium sulphate has been given by Dafert,[1] who has traced the various steps as follows:—

---

[1] *Z. a. C.*, 1883, **22**, 366.

(i) The sulphuric acid abstracts from the organic matter the elements of water; (ii) the sulphur dioxide produced by the action of the residual carbon on sulphuric acid exercises a reducing effect on the nitrogenous bodies present; (iii) from the nitrogenous bodies produced by the above reduction ammonia is formed by the action of an oxidizing body; (iv) the ammonia formed is at once fixed by the acid as ammonium sulphate. Asboth considers that the production of ammonia is greatly aided by the hydrogen, when in a nascent state, produced by the action of sulphuric acid or organic matter.

This idea is based on the fact that with those bodies which afford a deficit of hydrogen the formation of ammonia is imperfect.

The principal objections to the Kjeldahl process as originally carried out were the length of time required to decompose the nitrogenous substance and the small quantity of it that was used, thus rendering necessary the use of a large multiplier to get percentage of nitrogen (in addition to the frequent difficulty of obtaining a small, but representative, sample of a given substance). By the Kjeldahl-Gunning process the decomposition of the nitrogenous substance is greatly hastened and the use of 1-5 gm. for the determination is generally practicable. By the Kjeldahl-Gunning-Jodlbauer process substances containing some of their nitrogen in the form of nitrate are easily dealt with. Stronger standard solutions of acid are now used to absorb the ammonia distilled over, and the amount of the former that remains unneutralized is determined by titration with standard alkali solution of equivalent strength. In Kjeldahl's original method dry powdered potassium permanganate was added little by little to the hot liquid in the digestion flask, until a permanent green colour was produced, with the object of hastening the process of decomposition. This addition, however, has now been generally discarded, being totally unnecessary when the modified processes are used, and having been found, moreover, to give low results in some cases owing to the destruction of a portion of the ammonia.

The Kjeldahl-Gunning Process.

(Not applicable in the presence of nitrates.)

In this process potassium sulphate[2] is added to the sulphuric acid and substances in the digestion flask, by which means the oxidation of the organic matter is greatly facilitated. Acid salts are thus formed, which, by heating, lose water more easily than acid and act as decomposing and oxidising media in a manner resembling the action of sulphuric acid at high temperatures and under pressure. As a further help in the same direction the oxygen-carrying power of certain metallic oxides has been made use of. The oxides of copper and mercury were suggested by Wilfarth and Arnold respectively. Experience has shown that mercuric oxide, or even metallic mercury, gives the best results, and the latter is now widely, probably generally, used.

---

[1] *Z. a. C.*, 1885, **24**, 455

[2] Dried sodium sulphate answers quite as well and is cheaper.

Reagents and Apparatus Required.

1. Standard acid, which may be either sulphuric or hydrochloric ($^{N}/_{5}$ or $^{N}/_{2}$ acid is used).

2. Standard alkali, which may be ammonium, barium, sodium, or potassium hydroxide, of corresponding strength to the acid.

3. Strong sulphuric acid free from nitrates and giving a small "blank" allowance of nitrogen.

4. Metallic mercury, or mercuric oxide prepared in the wet way.

5. Potassium sulphate in rough powder (or dried sodium sulphate).

6. Granulated zinc.

7. Sodium (or potassium[1]) sulphide solution, containing 30 gm. of the fused salt in a litre.

8. A strong solution of caustic soda, free from nitrates, such that about 80 c.c. are required to neutralize 20 c.c. of the sulphuric acid (3 above) used. Each fresh lot should be tested and the number of c.c. required for 20 c.c. of acid marked on the bottle. About 5-10 c.c. more than this amount is added to the distillation flask for each 20 c.c. of acid used, due regard being paid to the probable amount of sulphuric acid destroyed during the decomposition of the substance.

9. Methyl orange, lacmoid, litmus, cochineal or rosolic acid solution as indicator. Methyl red, however, is stated by R. T. Thomson to be much superior to methyl orange for this purpose.

10. Digestion flasks, round-bottomed, holding about 200-250 c.c. preferably made of Jena glass, well-annealed and not too thick; the neck about ¾ inch wide and 3½-4 inches long.

11. Distillation flasks of hard Bohemian or Jena glass of conical shape, 600-850 c.c. capacity, fitted with a rubber stopper and a bulb above with curved delivery tube, to prevent the spray of the boiling alkaline liquid from being carried over into the condenser tubes. Copper distilling bottles or flasks are used by some operators for technical purposes with good results, but in this case it is advisable to put the soda into the vessel first, then to add the acid liquid.

12. The condenser. Owing to the undoubted solubility of glass in freshly distilled water containing ammonia, it is advisable to have the condenser tube made of pure block tin. This should be about three-eighths of an inch wide externally, and is connected with the bulb tube of the distilling flask with stout pure rubber tube. It is surrounded by either a metal or glass casing, through which a current of cold water is passed in the usual manner. It is very easy to fit up such an arrangement with the condenser tubes made entirely of glass sold by the dealers in chemical apparatus. The end of the condenser tube may be simply inserted into

---

[1] If potassium sulphide is used 40 gm. should be taken.

the neck of a flask containing the standard acid, or it may have a delivery tube connected by a rubber tube leading into a beaker. There is no necessity for dipping the delivery tube into the acid unless the temperature of the laboratory is very high.

For use in my own laboratory, where a large number of agricultural samples are examined, the form shown in Fig. 28 has been adopted and has been found to answer well.

The body of the condenser consists of an ordinary 10 gallon iron drum filled with water; the pure tin distilling tubes run through this at equal distances from each other, and emerge at the bottom of sufficient length to dip into the vessels containing the standard acid. With this arrangement there is no necessity for running water, and six distillations may be carried on simultaneously without fear of losing ammonia; the body of water is so great that the lower portion is quite cool after the distillations are finished. In case of extremely hot weather or in a very hot laboratory the cover may be removed and a lump of ice placed in the water if a large number of distillations are required.

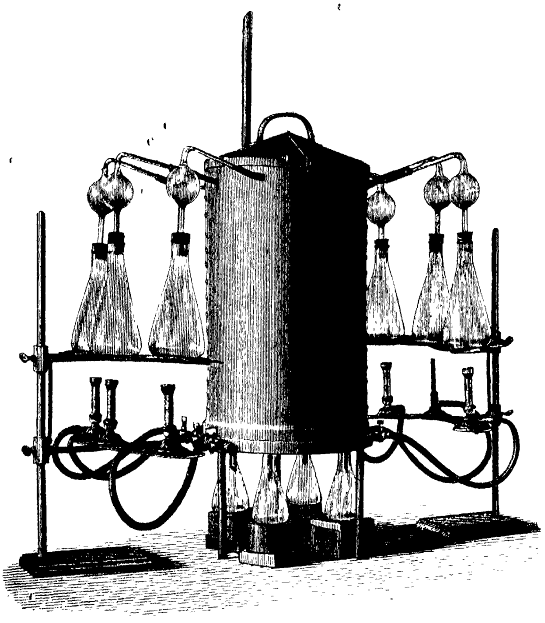

FIG. 28.

The distilling flasks are closed with rubber stoppers, and fitted with glass bulb tops as in Fig. 28. These are connected with the tin tubes by rubber joints, and supported on an iron frame over which is laid a strip of wire gauze. The Bunsen burners are of Fletcher's make with nickel gauze tops which give a smokeless flame of any desired size.

So well does this arrangement work that during many hundreds of distillations not one breakage has occurred due to the heating or the distillation. The tin condensing tubes do not in this case dip into the standard acid, as various experiments have proved it unnecessary unless the temperature of the laboratory is very high.

B. Dyer uses a tin condensing tube (air condenser) rising 15-18 inches vertically from the distilling flask, then bent downwards and fitting into a pear-shaped adapter (with large expansion to allow of varied pressure), whose narrowed end dips actually into the acid. The receiving flask should stand in a tank of running water.

13. A convenient stand for holding the digestion flasks is shown in Fig. 29. They rest in an oblique position and heat is applied by small Bunsen burners. With a little care the naked flame can be applied directly to the flask without danger. Some operators prefer to close the digestion flasks with a loosely fitting glass stopper elongated to a point, and having a balloon-shaped top. This aids in the condensation of any acid which may distil, but if the flasks are tolerably long in the neck, there is practically no loss of acid except as SO_2, which occurs in any case. It is almost needless to say that the digestion should be done in a fume closet with good draught.

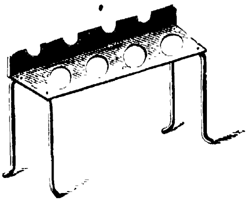

Fig. 29.

The Process. From 0·5-5 gm. of the substance, according to the percentage of nitrogen present, are put into a digestion flask, about 0·7 gm. of mercury added by means of a dropping tube marked to deliver that amount and kept for the purpose, then 20 c.c. of sulphuric acid (3)—or 30 c.c. if necessary, as in the case of some bulky vegetable substances. The flask—either with or without a loosely fitting hollow stopper made of thin glass[1] (see 13 above)—is placed in an inclined position on wire gauze in a convenient stand over a Bunsen burner, and heated, gently at first, till frothing has ceased. The heat is then raised until the acid boils briskly and the boiling continued for about 15 minutes. The flask is then momentarily removed to a cork mat, 7-10 gm. of potassium sulphate (5) added, and the boiling resumed. No further attention is required till the contents of the flask have become a clear liquid, which is colourless or at most has a very pale straw colour, the time occupied being usually under an hour. The flask is then allowed to cool and the contents are diluted with water and transferred to the distillation flask, the digestion flask being well rinsed and about 250 c.c. of water used altogether.[2] The proper quantity of caustic soda solution (8) is then added (according to the amount of sulphuric acid used to decompose the substance), then 25 c.c. of sodium sulphide solution (7), and a few pieces of granulated zinc, which, by generating hydrogen, prevents bumping. The flask is at once connected with the condenser and the contents are distilled till all ammonia has passed over into the receiving flask, into which has previously been measured an amount of standard acid more than sufficient to neutralise the ammonia distilled over.

---

[1] B. Dyer recommends this, and Lunge (*Techn. Meth. Anal.*, Vol. II, p. 376 and 471) states that it is necessary. As tending to prevent undue concentration of the acid liquid it is decidedly advantageous. See "Notes" on p. 90.

[2] Any heavy siliceous residue should be washed by decantation, not rinsed into the distillation flask, where it would cause heavy bumping, not to say a breakage.

This operation generally requires about 30 minutes. If the liquid froths badly a small piece of paraffin wax, about the size of a pea, should be added. The distillate is then titrated with standard alkali, either directly or by running in a level number of c.c. in excess and titrating residually.

Notes on the Process.—Care should be taken to prevent too great concentration of the boiling mixture in the digestion flask through loss of acid, as, in these circumstances, there is danger of a loss of ammonia by volatilization, owing to the high temperature attained. This was pointed out by P. A. W. Self,[1] who showed that this loss occurs when the temperature of the mixture of sulphuric acid and potassium sulphate rises above a certain point, and is very marked as the liquid approximates to the composition of potassium bisulphate. To avoid this loss it is recommended that the amount of sulphuric acid used should be such that at least 15 gm. remain in the free state at the end of the digestion process. Not more than 3·5 gm. of a cereal or other substance consisting chiefly of carbohydrates, or more than 3 gm. of a substance containing 5 to 10 per cent. of fat, should be digested with 25 c.c of sulphuric acid and 12 gm. of potassium sulphate. E. Carpiaux[2] confirms the above in every detail, and recommends that only moderate amounts of potassium sulphate should be used and that the digestion should not be unduly prolonged after the substance has been completely decomposed.

In the case of feeding cakes and substances containing saccharine constituents it is a good plan to place the mercury and about 10 c.c. of sulphuric acid in the digestion flask first, then to add the sample and finally the remainder of the 20 c.c. of sulphuric acid. The flask should then be heated gently, with occasional shaking, on the edge of a hot plate till frothing has ceased.

Cheese, milk, etc., give, after decomposition, solutions which froth badly in the distillation flask. To avoid this, Brown[3] recommends that the solution obtained after decomposition by sulphuric acid be diluted with water to about 100 c.c. and boiled briskly in the digestion flask until only about 40 c.c. remain. On transferring to the distillation flask, diluting, and adding caustic soda, etc., as usual, the distillation can be carried out without the least trouble.

In place of 0·7 gm. of mercury (or 1 gm. of mercuric oxide) 0·5 gm. of anhydrous copper sulphate may be used. It has been found, however, that mercury has the greatest effect on the oxidation, so that the decomposition requires appreciably less time than when copper sulphate is used

---

[1] *P. J.*, 1912, **88**, 384.

[2] *Ann. Chim. anal.*, 1913, **18**, 315.

[3] *C. N.*, 1910, **102**, 51.

(Smetham and others). Where mercury is used, sodium sulphide is added in order to precipitate the mercury as sulphide and so prevent the formation of mercuro-ammonium compounds, which would cause a deficit in the yield of ammonia.

A blank determination should be made by heating 1 gm. of pure cane sugar with 20 c.c. of sulphuric acid, mercury and potassium sulphate being added, etc., and the distillate received in 5 c.c. of $^{N}/_{5}$ acid. To this 5 c.c. of $^{N}/_{5}$ caustic soda are added, with a drop of methyl-orange or other indicator, and $^{N}/_{5}$ acid run in till the colour change takes place. With good acid 20 c.c. give "blanks" ranging from 0·1-0·3 c.c. of $^{N}/_{5}$ acid. The amount so found is, of course, deducted, in actual determinations, from the amounts of standard acid neutralized; and if more than 20 c.c. of acid have been used the blank to be deducted will be proportionately increased. The use of cane-sugar is to reduce any trace of nitrates that may be present in the sulphuric acid.

EXAMPLE: 2 gm. of bone-meal taken.

30 c.c. of $^{N}/_{5}$ acid measured into the receiving flask, and 5·5 c.c. of $^{N}/_{5}$ alkali were required after the distillation

30 − 5·5 = 24·5
less "blank" 0·3

24·2 : 2 = 12·1 = 3·39 per cent. N = 4·12 per cent. NH_3.

The Kjeldahl-Gunning-Jodlbauer Process for the Determination of Organic Nitrogen in the presence of Nitrates.

This modification was introduced to meet the difficulty caused by the loss of nitrogen when a nitrate is acted on by sulphuric acid. Many organic compounds capable of forming nitro-compounds in these circumstances were tried—e.g. phenol and benzoic acid—but salicylic was finally found to give the best results. The procedure is as follows:—

First mix in a beaker 30 c.c. of sulphuric acid (3) and 1 gm. of salicylic acid.[1] Next place in a digestion flask a weighed quantity of the substance to be analysed (usually 0·5-5 gm.)—no mercury being added at this stage. Now pour the acid in the beaker quickly into the flask, so as to cover the whole of the sample at once. Allow to stand for 10 minutes in the cold, with occasional shaking, taking care that the temperature does not rise appreciably. Should the flask become perceptibly warm it must be at once placed in cold water, or even, if necessary, in ice and water. At the end of 10 minutes 1 gm. of zinc dust[2] is added in small portions at a time, with shaking, then 0·7 gm. of mercury and the flask and contents heated gently till frothing is over. Potassium sulphate (7-10 gm.) is added and the process finished as described above (Kjeldahl-Gunning Process).

A "blank" with all reagents used is made as before.

---

[1] It is best to make the mixture immediately before use, not to make a quantity to form a stock solution.

[2] Granulated zinc or zinc filings will not answer. 5 gm. of crystallized sodium thiosulphate may be used in place of the zinc dust. It gives equally good results, but has the disadvantage of causing considerable frothing.

Theory of the Jodlbauer Process.—The theory of the process by which salicylic acid converts nitrates into ammonia is as follows:

1. When salicylic acid and sulphuric acid are added to a nitrate in the cold, the sulphuric acid takes up water and one of the hydrogen atoms of the salicylic acid is replaced by NO_2, forming nitro-salicylic acid. It is probably mononitro- and not dinitro- salicylic acid that is formed, thus

$$C_6H_5OHCO_2H + HNO_3 + H_2SO_4 = C_6H_4(NO_2)OHCO_2H + H_2SO_4 + H_2O.$$

2. When zinc dust is added the nascent hydrogen produced reduces the nitro- to amino- salicylic acid as follows:—

$$C_6H_4(NO_2)OHCO_2H + 3H_2 + H_2SO_4 = C_6H_4(NH_2)OHCO_2H + 2H_2O + H_2SO_4.$$

3. By the action of strong sulphuric acid and heat the amino-salicylic acid breaks up with the formation of ammonium sulphate, CO_2, SO_2 and water, as follows:

$$2C_6H_4(NH_2)OHCO_2H + 28H_2SO_4 = (NH_4)_2SO_4 + 14CO_2 + 27SO_2 + 32H_2O.$$

In place of a measured amount of standard acid in the flask used to receive the distillate in either of the above processes, L. W. Winkler[1] recommends boric acid as an absorption medium, the advantage being that the ammonia is afterwards titrated directly with standard hydrochloric acid. The method of procedure is as follows:—

The distillate (200-300 c.c.) from the ammoniacal liquid is passed into a cooled receiver containing 10 gm. of boric acid in 100 c.c. of distilled water. A narrow-necked receiver, e.g. a Soxhlet flask, is preferable, and the mouth should be closed with a wad. The receiver is cooled by water and the use of a condenser may be dispensed with. The distillate is titrated with $^{N}/_{10}$ or $^{N}/_{5}$ hydrochloric acid, using congo red or methyl orange as indicator. For great accuracy water free from CO_2 is used, a boric acid solution containing the same amount of indicator is used as a colour standard, *and the hydrochloric acid is standardized by distilling a weighed* quantity of pure ammonium *chloride with alkali* under similar conditions. Results of high accuracy were thus obtained.

For such products as *spent oxide*, etc. (where thiocyanates, ferrocyanides, and double cyanides such as $Fe_7(CN)_{18}$ are present) Knublauch gives the following details of procedure: 1 gm. of the sample, dried at 50° C., is treated with 10 c.c. of sulphuric acid, allowed to stand for 5 minutes, then heated gently for 20 minutes, and afterwards boiled for 10 minutes. About 0·25 gm. mercury (or 0·05 gm. CuO) is now added and the mixture boiled for 1 hour. Then dilute with water, add excess of NaOH, then 5 c.c. sodium sulphide solution as usual, and distil off the ammonia.

For the determination of nitrogen in nitro-substitution compounds, such as picric acid and nitro-derivatives of toluene, W. C. Cope[2] recommends the following modification, which, however, does not give good results with tetranitro-aniline, tetranitro-methylaniline and dinitro-naphthalene.

To about 0·5 gm. of the substance in a Kjeldahl digestion flask add a solution of 2 gm. of salicylic acid in 30 c.c. of 96 per cent. sulphuric acid and let stand in the cold, with occasional shaking, till the substance is dissolved. Then add 2 gm. of zinc dust, in small portions, with cooling. After standing for 1½ to 2 hours, with shaking at intervals of 10 to 15 minutes, the flask is left overnight, then heated over a small flame until fumes are no longer evolved. The solution is boiled for 1½ to 2 hours, 1 gm. of yellow mercuric oxide added, and again boiled for 1 to 1½ hour, cooled, 7·5 gm. of potassium sulphate and 10 c.c. of sulphuric acid added, and again boiled for 1½ to 2 hours. If the solution is not clear and almost colourless, 1 gm. more of potassium sulphate is added, and boiling continued for a further ½ to 1 hour. The solution is then transferred to a distillation flask, 85-90 c.c. of sodium hydroxide solution (750 gm. per litre), 25 c.c. of potassium sulphide solution (80 gm. per litre) and 1 gm. of granulated zinc added and the ammonia distilled off.

---

[1] *Z. a. C.*, 1913, **26**, 231 and 1914, **27**, 630.

[2] *J. Ind. Eng. Chem.*, 1916, **8**, 592.

7. Method of Ronchèse.[1]

This method depends on the fact that in the presence of a large excess of formaldehyde ammonium salts form hexamethylene-tetramine, $N_4(CH_2)_6$ (see under Formaldehyde). The liberated acid titrated directly with standard alkali gives a measure of the combined ammonia. The method is interesting, and obviates distillation, but is of limited scope. J. M. Wilkie[2] has improved it, and H. G. Bennett[3] has applied it to the determination of hide-substance in leather and tannery liquors.

ACETIC ACID.

$C_2H_4O_2$ = 60·032.

Acetic anhydride $C_4H_6O_3$ = 102·048.

In consequence of the discrepancies existing between the sp. gr. of strong acetic acid and its actual strength, the hydrometer readings are not reliable; but the volumetric determination is now rendered extremely accurate by using phenolphthalein as indicator, acetates of the alkalis and alkaline earths having a perfectly neutral behaviour to this indicator. Even coloured vinegars may be titrated when highly diluted. Where, however, the colour is too dark for this method to succeed, Pettenkofer's method of procedure is the best, and this is endorsed by A. R. Leeds.[4] The latter takes 50 c.c. of the vinegar and 50 c.c. of water with a drop of phenolphthalein, then adds $^N/_{10}$ baryta to slight excess. This causes the organic colouring matters to separate either in the cold or on warming, and the excess of baryta is then found by titration with $^N/_{10}$ acid and turmeric paper.

Several processes have at various times been suggested for the accurate and ready determination of acetic acid, among which is that of Greville Williams, by means of a standard solution of lime syrup. The results obtained were very satisfactory.

C. Mohr's process consists in adding to the acid a known excess of precipitated neutral and somewhat moist calcium carbonate. When the decomposition is as nearly as possible complete in the cold, the mixture must be heated to expel the CO_2 and to complete the saturation;

---

[1] *J. Pharm. Chem.* 1907, 611, and *Analyst*, 1907, **32**, 303.

[2] *J. S. C. I.* 1910, **29**, 6.

[3] *J. S. C. I.*, 1909, **28**, 291.

[4] *J. A. C. S.*, **17**, 741.

the residual carbonate is then brought upon a filter, washed with boiling water, treated with excess of normal acid and titrated back with alkali.

In testing the impure brown pyroligneous acid of commerce, this method has given fairly accurate results.[1]

The titration of acetic acid or vinegar may also be performed by the ammonio-cupric solution described on p. 56.

1. Free Mineral Acids in Vinegar.—Hehner has devised an excellent method for this purpose.[2]

Acetates of the alkalis are always present in commercial vinegar; and when such vinegar is evaporated to dryness, and the ash ignited, the alkalis are converted into carbonates having a distinct alkaline reaction on litmus; if, however, the ash has a neutral or acid reaction, some free mineral acid must have been present. The alkalinity of the ash is diminished in exact proportion to the amount of mineral acid added to the vinegar as an adulterant.

METHOD OF PROCEDURE: 50 c.c. of the vinegar are mixed with 25 c.c. of $^{N}/_{10}$ soda or potash, evaporated to dryness, and ignited at a low red heat to convert the acetates into carbonates; when cooled, 25 c.c. of $^{N}/_{10}$ acid are added; the mixture heated to expel CO_2, and filtered; after washing the residue, the filtrate and washings are exactly titrated with $^{N}/_{10}$ alkali; the volume so used gives the amount of mineral acid present in the 50 c.c. of vinegar.

1 c.c. $^{N}/_{10}$ alkali = 0·0049 gm. H_2SO_4 or 0·003647 gm. HCl.

If the vinegar contains more than 0·2 per cent. of mineral acid, more than 25 c.c. of $^{N}/^{10}$ alkali must be used to the 50 c.c. vinegar before evaporating and igniting.

2. Acetates of the Alkalis and Earths.—These salts are converted by ignition into carbonates, and can be then residually titrated with normal acid; no other organic acids must be present, nor must nitrates, or similar compounds decomposable by heat. 1 c.c. normal acid = 0·06 gm. acetic acid.

3. Metallic Acetates.—Neutral solutions of lead and iron acetates may be precipitated by an excess of normal sodium or potassium carbonate, the precipitate well boiled, filtered, and washed with hot water, the filtrate and washings made up to a definite volume, and an aliquot portion titrated with $^{N}/_{10}$ acid; the difference between the quantity so used and calculated for the original volume of alkali will represent the acetic acid.

If such solutions contain free acetic or mineral acids, they must be exactly neutralized previous to treatment.

If salts other than acetates are present, the process must be modified as follows:—

METHOD OF PROCEDURE: Precipitate with alkali carbonate in excess, exactly neutralize with hydrochloric acid, evaporate the whole or part to dryness, ignite to convert the acetates into carbonates, then titrate residually with normal acid. Any organic acid other than acetic will, of course, record itself in terms of acetic acid.

---

[1] A. R. Leeds (*loc. cit.*) has not found this method to answer, which I think must be due to using dried calcium carbonate I have only used it for commercial wood acid, and the figures obtained by me were the highest among several other methods: but it is important to mention that the $CaCO_3$ should not be thoroughly dried, and that its alkalinity should be known.

[2] *Analyst,* 1875, 1, 165.

4. Commercial Acetate of Lime.—The methods just described are often valueless in the case of this substance, owing to the presence of tarry matters, which readily produce an excess of carbonates.

Fresenius[1] adopts the following process for tolerably pure samples.

Method of Procedure: 5 gm. are weighed and transferred to a 250 c.c. flask, dissolved in about 150 c.c. of water, and 70 c.c. of normal oxalic acid added; the flask is then well shaken, and filled to the mark, 2 c.c. of water are added to allow for the volume occupied by the precipitate, the whole is again well shaken and left to settle. The solution is then filtered through a dry filter into a dry flask, the volume so filtered must exceed 200 c.c

100 c.c. are first titrated with normal alkali and litmus; or, if highly coloured, by help of litmus or turmeric paper; the volume used multiplied by 2·5 will give the volume for 5 gm

Another 100 c.c. are precipitated with solution of pure calcium acetate in slight excess, warmed gently, the precipitate allowed to settle somewhat, then filtered, well washed, dried, and strongly ignited, in order to convert the oxalate into calcium carbonate or oxide, or a mixture of both. The residue so obtained is then decomposed with excess of normal acid, and titrated residually with normal alkali. By deducting the volume of acid used to neutralize the precipitate from that of the alkali used in the first 100 c.c., and multiplying by 2·5, there is obtained the volume of alkali expressing the weight of acetic acid in the 5 gm. of acetate.

In the case of very impure and highly coloured samples of acetate, it is only possible to determine the acetic acid by distillation with phosphoric acid and water and then titrating the acid direct with $^N/_{10}$ alkali, each c.c. of which represents 0·006 gm. acetic acid.

The distillation is best carried out as suggested by Gladding.[2]

Method of Procedure: 2 gm. of the sample are distilled with 30 c.c. of water and 10 c.c. of phosphoric acid sp. gr. 1·70 in a long-necked flask of 300 c.c. capacity for 1½ hour, the volume being kept constant by the continuous addition of CO_2-free water, and the distillate collected in standard alkali solution. Concordant results are obtained with varying concentrations of acetate of lime and phosphoric acid. A current of steam, as used by Fresenius and Grunhut, who condemned the method, leads to faulty results.

Weber[3] has devised a ready and fairly accurate method of determining the real acetic acid in samples of acetate of lime, based on the fact that acetate of silver is insoluble in alcohol.

Method of Procedure: 10 gm. of the sample in powder are placed in a 250 c.c. flask, a little water added, and heated till all soluble matters are extracted, cooled, and made up to the mark; 25 c.c. are then filtered through a dry filter, put into a beaker, 50 c.c. of absolute alcohol added, and the acetic acid at once precipitated with an alcoholic solution of silver nitrate. The silver acetate, together with any chloride, sulphate, etc., separates free from colour. The precipitate is brought on a filter, well washed with 60 per cent. alcohol till the free silver is removed; precipitate is then dissolved in weak nitric acid, and titrated with $^N/_{10}$ salt solution. Each c.c. represents 0·006 gm. acetic acid.

---

[1] *Z. a. C.*, **13**, 153.

[2] *J. Ind. and Eng. Chem.*, 1909, **1**, 250.

[3] *Z. a. C.*, **24**, 614

Several trials made in comparison with the distillation method with phosphoric acid gave practically the same results.

5. Acetic Anhydride, $C_4H_6O_3$.—Acetic anhydride is hydrolysed by water at ordinary temperatures.

$$C_4H_6O_3 + H_2O = 2C_2H_4O_2.$$

Thus, this substance may be assayed by agitating a known weight with CO_2-free water, and titrating the acetic acid formed with standard barium hydroxide solution and phenolphthalein.

Where it is required to determine acetic acid and anhydride in the presence of each other, as, e.g. in a sample of anhydride which contains acetic acid as an impurity, the following procedure may be adopted.

METHOD OF PROCEDURE: Place a known weight of the sample, contained in a small glass bulb, in a known volume of standard $Ba(OH)_2$ solution in excess, say, 250 c.c. $^N/_{10}$ alkali solution for about 1 gm. of the sample, in a flask. Connect the flask with a reflux condenser fitted with a soda-lime tube, and warm gently until the anhydride is dissolved. Disconnect the flask, and titrate the excess of alkali over the acetic acid formed with standard hydrochloric acid and phenolphthalein.

In the weight of sample taken for analysis (w) if a = acetic acid present as the free acid, and b = anhydride present as such, then $w = a + b$ (1), and the acetic acid formed by hydrolysis of b is seen to be

$$\frac{2C_2H_4O_2}{C_4H_6O_3}b = \frac{120{\cdot}064}{102{\cdot}048}b = 1{\cdot}1766\ b.$$

Thus, the total acetic present after hydrolysis, $v = a + 1{\cdot}1766\ b$ (2). Resolving (1) and (2), $b = (v - w)\frac{1}{{\cdot}1766} = 5{\cdot}663\ (v - w)$,

v being given by the acetic acid equivalent of the barium hydroxide neutralized by the total amount of acetic acid present after hydrolysis.

Assay of Acetic Anhydride by the Aniline Method[1] (Menschutkin and Vasilieff, 1889). International Method, 1911, in connection with the analysis of crude glycerol.

METHOD OF PROCEDURE: Into a weighed stoppered vessel, containing 10-20 c.c. of water, run about 2 c.c. of the anhydride, replace stopper and weigh; allow to stand, with occasional shaking for several hours, till all anhydride is hydrolysed, then dilute to about 200 c.c., add phenolphthalein, and titrate with $^N/_1$ caustic soda (free from carbonate). This gives the total acidity due to free acetic acid in the sample and to the acetic acid formed from the anhydride. (Note.—It is preferable to perform the hydrolysis in a known excess of $^N/_1$ soda, titrating back.)

Into a stoppered vessel containing a known weight of recently-distilled aniline (from 10-20 c.c.), and standing in ice-cold water, run about 2 c.c. of the sample, replace stopper, agitate, allow to stand in the cooling water a few minutes, and weigh. Add about 100 c.c. of cold water, and titrate the acidity as before.

---

[1] *Analyst*, 1911, **36**, 314; Orton and Jones, *J. C. S.*, 1912, **101**, 1781; Hewitt and Lumsden, *J. S. C. I.*, 1916, **35**, 210; Radcliffe and Medofski, *J. S. C. I.*, 1917, **36**, 628; Richmond, *Analyst*, 1917, **42**, 133.

The second titration gives the acidity due to the original, preformed, acetic acid plus one-half the acid due to anhydride (the other half having formed acetanilide). The second result is subtracted from the first (both calculated for 100 gm. of sample), and the result doubled = the c.c. of N/1 soda consumed per 100 gm. of sample.

1 c.c. N/1 soda = 0·051 gm. acetic anhydride.

In this reaction acetanilide is formed thus :—

$$(CH_3 . CO)_2O + C_6H_5NH_2 = C_6H_5 . NH . COCH_3 + CH_3COOH.$$

BORIC ACID AND BORATES.

Boric anhydride B_2O_3 = 69·8.
Boric acid H_3BO_3 = 61·924.
Sodium borate $Na_2B_4O_7$ = 201·6.
„ „ (cryst.) $Na_2B_4O_7, 10H_2O$ = 381·76.

The volumetric determination of boric acid[1] formerly presented great difficulties, but these have now been overcome by the following methods, which are due to R. T. Thomson.[2]

Method 1.—Titration of a borate by a mineral acid, using as indicator methyl orange, which is unaffected by boric acid. In the case of borax the following reaction takes place :

$$\begin{array}{l} \underset{\substack{201·6 \\ (100·8)}}{\underset{|}{Na_2B_4O_7}} + \underset{\substack{98·076 \\ (49·038).}}{\underset{|}{H_2SO_4}} + 5H_2O = Na_2SO_4 + 4H_3BO_3 \end{array}$$

Hence 1 litre of N . H_2SO_4 = 100·8 gm. $Na_2B_4O_7$
or 1 c.c. N . H_2SO_4 = 0·1008 gm. $Na_2B_4O_7$
= 0·19088 gm. $Na_2B_4O_7, 10H_2O$.

EXAMPLE : 1·683 gm. of sodium borate dissolved in 50 c.c. of water required 16·7 c.c. of normal acid.

$$\frac{16·7 \times ·1008 \times 100}{1·683} = \frac{168·34}{1·683} = 100·02 \text{ per cent. } Na_2B_4O_7.$$

Method 2. Titration of free boric acid by standard alkali in presence of glycerol, using as indicator phenolphthalein, to which boric acid behaves as a monobasic acid. Carbon dioxide must not be present. The following reaction takes place :

$$\underset{61·924}{\underset{|}{H_3BO_3}} + \underset{40·008}{\underset{|}{NaOH}} = NaBO_2 + 2H_2O.$$

Hence, 1 litre of N . NaOH = 61·924 gm. H_3BO_3
or 1 c.c. N . NaOH = 0·061924 gm. H_3BO_3
= 0·504 gm. $Na_2B_4O_7$
= 0·09544 gm. $Na_2B_4O_7, 10H_2O$.

---

[1] Theoretical considerations indicate that boric acid might possibly be titrated directly with tolerable exactness by the selection of a suitable indicator. Tropaeolin O, in 0·04 per cent. solution, has been found to succeed with pure solutions of boric acid, using 0·5 to 1 c.c. of the indicator. If the solution be saturated with sodium chloride, very dilute concentrations of boric acid may be titrated with as much accuracy as stronger solutions (Prideaux, *Z. anorg. C.*, 1913, **83**, 362).

[2] *J. S. C. I.*, 1893, **12**, 132.

Method of Procedure: To the aqueous solution of a borate add methyl orange and run in normal acid from a burette till the solution just becomes pink. Boil for a short time to expel CO_2, cool, and add $^N/_1$ or $^N/_5$ soda till the solution just assumes a yellow tinge (an extra drop of methyl orange solution having previously been added if necessary). At this stage all the boric acid will be in the free state, as shown by equation given under Method 1. Add glycerin in such proportion that the solution after titration will contain at least 30 per cent., then phenolphthalein and run in $^N/_1$ or $^N/_5$ soda solution from a burette until a permanent pink colour is produced. If necessary, more glycerin may be added during the titration. The boric acid is calculated by means of the factors given above.

In the case of boric acid of commerce, which generally contains salts of ammonia, 1 gm. may be dissolved in hot water, a slight excess of sodium carbonate added, and the solution boiled down to about half its bulk to expel ammonia. Any precipitate which appears may then be filtered off, and the filtrate titrated as already described.

The method may also be applied to boracite and borate of lime by dissolving 1 gm. of either of these minerals in dilute hydrochloric acid with the aid of heat, nearly neutralizing with caustic soda, boiling to expel CO_2, cooling, exactly neutralizing to methyl orange, and continuing the determination as in borax. If much iron is present, however, it should be removed by a preliminary treatment with sodium carbonate and removal of oxide of iron as well as the carbonates of calcium and magnesium by filtration.

L. C. Jones[1] has based a method of titrating boric acid upon the fact that when a solution of the acid is mixed with one of mannitol, a much stronger acidic character is developed from the boric acid than it naturally possesses (a similar effect occurs with glycerin), and further, that boric acid alone in solution in moderate amount has not the slightest action on a solution containing potassium iodide and iodate. Therefore, if a given solution containing boric acid be mixed with iodide and iodate, the acid set free by addition of a mineral acid, and the free iodine so produced exactly destroyed by thiosulphate, there results a colourless liquid containing the boric acid in a free state and ready to be titrated by any convenient method.

Method of Procedure: The solution, about 50 c.c., containing the boric compound and about 0·1 gm. of boric acid, is acidified distinctly with hydrochloric acid, but any large excess must be removed with soda. 5 c.c. of a 10 per cent. solution of barium chloride are then added. In a separate beaker the iodide and iodate mixture, say 10 c.c. of a 25 per cent. solution of iodide and the same volume of a saturated solution of iodate, together with starch indicator is placed—the quantity must be sufficient to liberate an amount of iodine equivalent at least to the free HCl in the boric solution, the colour of the starch iodide which is usually liberated from this mixture is removed by a dilute solution of sodium thiosulphate. To this neutral solution of iodide and iodate a single drop of the boric solution is added by a glass rod; if a blue colour appears it is evident that the boric solution is acid with free HCl and the boric acid is in a free condition. The solutions are then mixed and the free iodine removed by cautious addition of thiosulphate. The mixture is then colourless and contains only starch, neutral chloride, potassium tetrathionate, iodide and iodate, with all the B_2O_3 in a free state. Any CO_2 will have been removed by the barium chloride.

---

[1] *J. A. C. S.*, 1898, **20**, 147-153.

The titration is now begun by adding a few drops of phenolphthalein and $^N/_5$ caustic soda run in from the burette until a strong red colour is shown; a pinch of mannitol is then thrown in which bleaches the colour, more soda and more mannitol are in turn added until the colour is permanent. As a rule 1 or 2 gm. of mannitol suffice for a determination. The amount of B_2O_3 is calculated on the assumption that under the above-mentioned conditions 1 mol. of the acid requires 2 mol. of sodium hydroxide. Test analyses on calcium borate and colemanite gave satisfactory results and within a very short time. Silicates and fluorides do not interfere, but ammonium salts must be removed by boiling with alkali previous to adopting the process, owing to their well known effect on the indicator.

Schwartz[1] recommends the glycerin method in the case of boracite to be carried out as follows:—

1 or 2 gm. of the finely powdered material are mixed with 5 to 10 c.c. of strong hydrochloric acid, made up to about 50 or 100 c.c. with water, and digested with stirring for several hours at ordinary temperature. The process may be hastened by heating, but in that case a reflux condenser may be necessary to avoid loss of boric acid. In either case the liquid is filtered, residue washed, and the filtrate rendered exactly neutral to methyl orange with $^N/_5$ soda (free from CO_2). The volume is made up to 100 or 200 c.c., then 25 or 50 c.c. mixed with the same volume of absolutely neutral glycerin, diluted somewhat, then titrated with phenolphthalein and $^N/_5$ soda.

Boric Acid in Milk, Butter, and other Foods.—R. T Thomson.[2] 1 to 2 gm. of sodium hydrate are added to 100 c.c. of milk, and the whole evaporated to dryness in a platinum dish. The residue is cautiously but thoroughly charred, heated with 20 c.c. of water, and hydrochloric acid added drop by drop until all but the carbon is dissolved. The whole is transferred to a 100 c.c. flask, the bulk not being allowed to exceed 50 or 60 c.c., and 0·5 gm. dry calcium chloride added. To this mixture a few drops of phenolphthalein are added, then a 10 per cent. solution of caustic soda, till a permanent slight pink colour is perceptible, and finally 25 c.c. of lime-water. In this way all the P_2O_5 is precipitated as calcium phosphate. The liquid is made up to 100 c.c. thoroughly mixed and filtered through a dry filter. To 50 c.c of the filtrate (equal to 50 c.c. of the milk) normal sulphuric acid is added till the pink colour is gone, then methyl orange, and the addition of the acid continued until the yellow is just changed to pink. $^N/_5$ caustic soda is now added till the liquid assumes the yellow tinge, excess of soda being avoided. At this stage all acids likely to be present exist as salts neutral to phenolphthalein, except boric acid (which, being neutral to methyl orange, exists in the free condition), and a little CO_2, which it is absolutely necessary to expel by boiling for a few minutes. The solution is cooled, a little phenolphthalein added, and as much glycerin as will give at least 30 per cent. of that substance in the solution, then titrated with $^{N}/_{5}$ caustic soda till a distinct permanent pink colour is produced. Each c.c. of the soda is equal to 0·0124 gm. crystallized boric acid. A series of experiments with this process showed that no boric acid was precipitated with the phosphate of lime so long as the solution operated upon did not contain more than 0·2 per cent of crystallized boric acid, but when stronger solutions were tested, irregular results were obtained. The charring of the milk is apt to drive off boric acid, but by carefully carrying the incineration only so far as is necessary to secure a residue which will yield a colourless solution, no appreciable loss occurs.

---

[1] *Chem. Zeit.*, 1899, 497.

[2] *Glasgow City Anal. Soc. Repts.*, 1895, p. 3.

There is no doubt that CO_2 must be got rid of in titrating boric acid with phenolphthalein, and hence it is necessary to boil the solution. Some operators therefore do this in a flask with upright condenser to avoid the loss of boric acid. It is doubtful, however, whether by this confined escape, the gas is got rid of as easily as is thought. L. de Koningh[1] gives the results of experiments made in this manner, and shows that a dilute solution of the acid may be boiled even up to fifteen minutes in an open vessel (which is longer than necessary), with a loss of a very faint trace of the acid The same operator also advocates the removal of phosphoric acid, which is nearly always present in foods, by adding a slight excess of sodium carbonate to the boric acid liquid, then cautiously adding calcium chloride, this precipitates any phosphate and the excess of carbonate, while the borate in very dilute solution is not affected. On now adding a solution of ammonium carbonate containing an excess of free ammonia the excess of lime is precipitated. By boiling the clear solution with excess of sodium carbonate the ammonium compounds are quickly expelled, and the titration may be carried on as before described.

A new process is also described in the same article by which the boric acid may be determined after the removal of the P_2O_5 by means of magnesia mixture; the filtrate is mixed with excess of sodium carbonate and heated, the precipitate of magnesia is removed by filtration, the filtrate evaporated to dryness to render the rest of the magnesia insoluble, and the residue is then treated with a little water and filtered. The boric acid may then be titrated according to Thomson's glycerin method. As a test experiment, 0·1 gm. of boric acid was dissolved in aqueous soda, then mixed with 100 gm. of oatmeal and incinerated; from the ash, 0·095 gm. of boric acid was recovered.

A rapid method for determining boric acid in *BUTTER* has been worked out by H. Droop Richmond and J. B. P. Harrison.[2] 25 gm. of the butter are weighed out into a beaker, and 25 c.c. of a solution containing 6 gm. of milk sugar and 4 c.c. of normal sulphuric acid in 100 c.c. are added. The beaker is placed in the water oven until the fat has just melted and the mixture is well stirred. After allowing the aqueous portion to settle for a few minutes 20 c.c. are pipetted out, a little phenolphthalein added, brought to the boiling point, and titrated with semi-normal caustic soda until a faint pink colour just appears. 12 c.c. of neutral glycerin are now added, and the further titration carried on till a pink colour appears. The difference between the two titrations multiplied by 0·0368 gives the amount of boric acid in 20 c.c., and this multiplied by

---

[1] *J. A. C. S.*, 1897, **19**, 385.

[2] *Analyst*, 1902, **27**, 179.

$$\frac{100 + \text{percentage of water in the butter}}{20}$$

will give the percentage of boric acid. The determination is not affected by the phosphoric or butyric acid, or milk sugar present in the butter.

A quick method for the determination of boric acid in *MILK* and *CREAM* is due to Richardson and Walton.[1] It has the advantage of obviating the loss of boric acid which is liable to occur, in spite of the addition of soda, when fatty solids are charred, as in Thomson's method.

METHOD OF PROCEDURE. 5 c.c. of a 5 per cent. solution of copper sulphate are added to 50 c.c. of milk or 10 gm. of cream mixed with 40 c.c. of water. The mixture is well stirred, heated to boiling for a few seconds, and filtered, the precipitate being well washed four or five times with boiling water. To the cold filtrate 2 c.c. of a 1 per cent. neutralized solution of phenolphthalein are added, and $^{N}/_{10}$ soda run in until a definite blue shade appears. The usual proportion of glycerin is then added, and the titration with soda continued until the blue shade again appears. A very little practice enables the right point to be reached. Under these conditions, 1 c.c. $^{N}/_{10}$ NaOH = 0·0071 gm. boric acid

CARBONIC ACID AND CARBONATES.

ALL carbonates are decomposed by strong acids; the carbonic acid which is liberated splits up into water and carbonic anhydride (CO_2), which latter escapes in the gaseous form.

It will readily be seen, from what has been said previously as to the determination of the alkaline earths, that carbonic acid in combination can be determined volumetrically with a very high degree of accuracy (see p. 73).

The carbonic acid to be determined may be brought into combination with either calcium or barium, these bases admitting of the firmest combination as neutral carbonates.

If the carbonic acid exist in a soluble form as an alkali monocarbonate, the decomposition is effected by the addition of barium or calcium chloride as before directed; if as bicarbonate, or a compound between the two, ammonia must be added with either of the chlorides.

As solution of ammonia frequently contains traces of CO_2, this must be removed by the aid of barium or calcium chloride previous to use.

---

[1] *Analyst*, 1913, **38**, 110.

1. Carbonates Soluble in Water.

It is necessary to remember that when calcium chloride is used as the precipitant in the cold amorphous calcium carbonate is first formed; and as this compound is sensibly soluble in water, it is necessary to convert it into the crystalline form. In the absence of free ammonia this can be accomplished by boiling. When ammonia is present, the same end is obtained by allowing the mixture to stand for eight or ten hours in the cold, or by heating for an hour or two to 70-80° C. With barium the precipitation is regular.

Another fact is that when ammonia is present, and the precipitation occurs at ordinary temperatures, ammonium carbamate is formed and the barium or calcium carbonate is only partially precipitated. This difficulty is overcome by heating the mixture nearly to boiling for a couple of hours, and is best done by passing the neck of the flask through a retort ring, and immersing the flask in boiling water.

When caustic alkali is present in the substance to be examined, it is advisable to use barium as a precipitant; otherwise, for all volumetric determinations of CO_2 calcium is to be preferred, because the precipitate is much more quickly and perfectly washed than the barium compound.

Example: 1 gm. of pure anhydrous sodium carbonate was dissolved in water, precipitated while hot with barium chloride, the precipitate allowed to settle well, the clear liquid decanted through a moist filter, more hot water containing a few drops of ammonia poured over the precipitate, this treatment being repeated so that the bulk of the precipitate remained in the flask, being washed by decantation through the filter; when the washings showed no trace of chlorine, the filter was transferred to the flask containing the bulk of the precipitate, and 20 c.c. of normal nitric acid added, then titrated back with normal alkali, of which 1·2 c.c. was required = 18·8 c.c. of acid; this multiplied by 0·022, the coefficient for carbonic acid, gave 0·4136 gm. CO_2 = 41·36 per cent., or multiplied by 0·053, the coefficient for sodium carbonate, gave 0·9964 gm. instead of 1 gm.

2. Carbonates Soluble in Acids.

It sometimes occurs that substances have to be examined for carbonic acid which do not admit of being treated as above described, such, for instance, as white lead, calamine, carbonates of magnesia, iron, and copper, cements, mortar, and many other substances. In these cases the carbonic acid must be evolved from the combination by means of a stronger acid, and conducted into an absorption apparatus containing ammonia, then precipitated with calcium chloride, and titrated as before described.

The form of apparatus (fig. 30) affords satisfactory results.

Method of Procedure: The weighed substance from which the carbonic acid is to be evolved is placed in *b* with a little water; the tube *d* contains strong hydrochloric acid, and *c* broken glass wetted with ammonia free from carbonic acid. The flask *a* is about one-eighth filled with the same ammonia; the bent tube must not enter the liquid. When all is ready and the rubber stoppers tight, warm the flask *a* gently so as to fill it with vapour of ammonia, then open the clip and allow the acid to flow gradually upon the material, which may be heated until all carbonic acid is apparently driven off; then by boiling and shaking the last traces can be evolved, and the operation ended. When cool, the apparatus may be opened, the end of the bent tube washed into *a*, and also a good quantity of boiled distilled water passed through *c*, so as to carry down any ammonium carbonate that may have been formed. Then add solution of calcium chloride, boil, filter, and titrate the precipitate as before described.

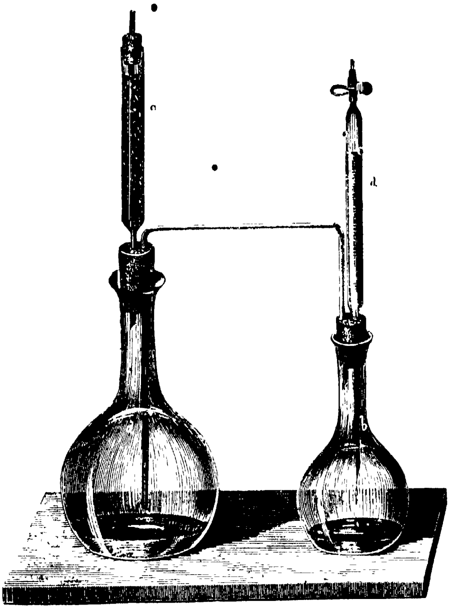

FIG. 30.

During the filtration, and while ammonia is present, there is a great avidity for carbonic acid, therefore boiling water should be used for washing, and the funnel kept covered with a small glass plate.

In many instances CO_2 may be determined by its equivalent in chlorine with $^N/_{10}$ silver and chromate, as on page 149.

3. Carbonic Acid Gas in Waters, etc.

The carbonic acid existing in waters as neutral carbonates of the alkalis or alkaline earths may very elegantly and readily be titrated directly by $^N/_{10}$ acid (see Water Section).

Detection of Free Carbon Dioxide in Water. L. W. Winkler.—[1] The presence of free carbon dioxide in moderately hard waters may be detected by adding 2 drops of 10 per cent. copper sulphate solution to 100 c.c. of the water. If free CO_2 is absent, the water becomes turbid, but if present the water remains clear. If the clear solution is shaken with air, the CO_2 is expelled and a turbidity is produced; if a turbidity does not develop under these conditions, the water contains humic acid or much organic matter. The test fails, however, in the case of soft waters, but free CO_2 may be detected in these waters by adding 10 drops of 1 per cent. alizarin solution in alcohol to 100 c.c. of the water. A blue-red coloration indicates the absence of free CO_2, a copper-red coloration, a small quantity; a reddish-yellow coloration, a moderate quantity; and a yellow coloration, a large quantity of the gas.

Well or spring water, and also mineral waters, containing free carbonic acid gas, can be examined by collecting measured quantities of them at their source, in bottles containing a mixture of calcium and ammonium chlorides, afterwards heating the mixture in boiling water for one or two hours, and titrating the precipitate as before described.

Pettenkofer's method with caustic baryta or lime is in general use. Lime water may be used instead of baryta with equally good results, but care must be taken that the precipitate is crystalline.

The principle of the method is that of removing all the carbonic acid from a solution, or from a water, by excess of baryta or lime water of a known strength; and, after absorption, determining the excess of baryta or lime by titration with $\frac{N}{10}$ acid and turmeric paper.

The following course is the best to be pursued in this method for ordinary drinking waters not containing large quantities of carbonic acid:—

METHOD OF PROCEDURE: 100 c.c. of the water are put into a flask with 3 c.c. of strong solution of calcium or barium chloride, and 2 c.c. of saturated solution of ammonium chloride, 45 c.c. of baryta or lime water, the strength of which has been previously ascertained by means of decinormal acid, are then added, the flask well corked and put aside to settle, when the precipitate has fully subsided, pipette 50 c.c. of the clear liquid into a beaker, and titrate it with decinormal acid. The quantity required must be multiplied by 3, there being 50 c.c. only taken; the number of c.c. so found must be deducted from the original quantity required for the baryta or lime solution added; the remainder multiplied by 0·0022 will give the weight of carbonic acid existing free and as bicarbonate in the 100 c.c.

The addition of the barium or calcium chloride and ammonium chloride is made to prevent any irregularity which might arise from alkali carbonates or sulphates, or from magnesia.

A more accurate method of determining CO_2 in its various states of existence in drinking waters has been used for some years past. It is described by C. A. Seyler.[2]

Whatever may really be the condition under which CO_2 exists in natural waters, and there is difference of opinion on the point, it is sufficient for all practical purposes to assume that it occurs in three forms, namely: first, as monocarbonates of alkalis or alkaline earths; second, as bicarbonates of the same; and third, as free CO_2. Seyler proposes to distinguish the first as fixed and the two others as volatile

---

[1] *Z. angew. C.*, 1915, **28**, 376.

[2] *C. N.*, 1894, **70**, 104; *Analyst*, 1897, **22**, 312.

CO_2, inasmuch as this gas existing as bicarbonate may be almost, and the free gas completely, dispelled by boiling. On the assumption that the half-bound acid (i.e. as bicarbonate) is equal to the combined, the free CO_2 may be determined by subtracting the combined from the volatile as found by Pettenkofer's process—this, however, is inaccurate with small quantities and tedious. What is required is a method of determining the free CO_2 independently.

Pettenkofer's method has been modified by Trillich, Lunge, and Seyler, and the modifications have been carefully investigated by Ellms and Beneker,[1] who have come to the conclusion that Seyler's method is the most accurate.

The essential details of the process are as follows:—

The free carbonic acid is determined by titrating 100 c.c. of the sample with N/20 sodium carbonate, using not too little phenolphthalein as indicator (say 25-30 drops). The colour vanishes rather slowly towards the end, and the standard carbonate is added till a permanent faint pink is obtained.

$$CO_2 + H_2O + Na_2CO_3 = 2NaHCO_3.$$

For accurate results the titration must be repeated, running in nearly the right amount at once and then finishing drop by drop.

METHOD OF PROCEDURE: 1. The titration can conveniently be performed in a Nessler cylinder, approximately 18 cm. long by 3 cm. in diameter, graduated for 50 and 100 c.c. The stirring rod is bent at its lower end into the form of a circle, and then turned so as to stand at right-angles to the rod. A comparison cylinder containing the same amount of water as the titrating cylinder is found to aid in the determination of the end-point.

2. The larger part of the sodium carbonate solution should be added quickly, and the strong pink colour formed should be discharged by stirring and mixing with the rod. The titration can then be cautiously completed, until colour remains permanent. The sodium carbonate solution should be prepared with freshly ignited sodium carbonate, and with air-free water. The exposure of this solution to the air should be avoided as much as possible, as sodium bicarbonate is readily formed, which renders it useless for this titration where accurate results are desired.

3. With waters that are high in free and half-bound carbonic acid it is better to use less than 100 c.c. for the titration. With such a water, care is necessary in transferring the sample to the cylinder in order to avoid loss of CO_2. Too vigorous stirring of the water is also to be avoided for the same reason.

The fixed carbonic acid, from which the half-bound acid is estimated, is determined according to the method of Hehner (*vide* Water Analysis). Seyler uses methyl orange as the indicator for this titration, but lacmoid is preferable.

In the absence of free CO_2 in a water, the half-bound may equal the fixed, in which case it would be neutral to phenolphthalein. If, however, the water is alkaline to phenolphthalein, the half-bound CO_2

---

[1] J. A. C. S., 1901, 23, 105.

does not equal the fixed; or, in other words, a portion of the carbonates of the bases exist in solution without the assistance of any half-bound CO_2. In such a case the half-bound acid is obtained by first determining the fixed CO_2 by means of lacmoid. From this is deducted an amount of CO_2 equal to twice the quantity indicated by the acid required to discharge the pink colour produced by phenolphthalein. The difference is the amount of half-bound CO_2 which is present. These titrations may be made on the same sample, in which case the "phenolphthalein alkalinity" is first determined and then followed by the titration with lacmoid; or they may be made on separate samples.

The principles upon which the above procedure is based have been pointed out above.

Seyler gives the following formulæ:—

1. For waters neutral or acid to phenolphthalein (the commonest case).

Let p = no. of c.c. of $^N/_{20}$[1] sodium carbonate used to produce a pink colour with phenolphthalein in 100 c.c. of the water; and
m = no. of c.c. of $^N/_{20}$ sulphuric acid required to obtain the end-point with methyl orange or lacmoid in the same volume of water.

Then, Free CO_2 = $1·1\,p$ parts per 100,000
Fixed CO_2 = $1·1\,m$,, ,, ,,
Volatile CO_2 = $1·1\,(m + p)$,, ,,
Total CO_2 = $1·1\,(2m + p)$,, ,,

2. For waters alkaline to phenolpthalein[2] (as sometimes happens in perfectly natural waters).

Let p' = no. of c.c. of $^N/_{20}$ acid required to be run into 100 c.c of the water tinted with phenolphthalein to discharge the colour;
m = no. of c.c. of $^N/_{20}$ acid required to be further added to the above solution, to which methyl orange or lacmoid has been added, till the end-point is obtained.

Then, Fixed CO_2 = $1·1\,m$ parts per 100,000
Volatile CO_2 = $1·1\,(m - 2p')$,, ,,
Total CO_2 = $1·1\,(2m - 2p')$,, ,,

(We have $2p'$ here because the same amount of acid corresponds to twice as much CO_2 when phenolphthalein is used as when methyl orange is used.)

R. Czensny[3] observes that in the above titration it is necessary to vary the amount of indicator in proportion to the amount of bicarbonate present. This is most conveniently attained by adding a substantial quantity of phenolphthalein to the standard sodium carbonate solution. His method is as follows:—The standard $^N/_{20}$ soda solution is made by dissolving 2·6525 gm. of pure sodium carbonate and 2·5 gm. of phenolphthalein in boiled distilled water and making up to a litre. 100 c.c. of the water are titrated with this solution to a permanent pink. He found that 0·52 c.c. of the $^N/_{20}$ alkali was required before any indication was shown, and this amount is deducted from the number of c.c. used as a constant correction for the zero point of the titration. The remainder is multiplied by the factor 1·22 (instead of the theoretical 1·1).

---

[1] 1 c.c. = 1·1 mgm. CO_2 = 2·5 mgm. $CaCO_3$.

[2] Such waters can, of course, contain no free CO_2.

[3] *Z. a. C.*, 1919, **58**, 1-12.

There is a third case in which free CO_2 might exist in a solution containing free mineral acid, and for which Seyler has given a method with its corresponding formulæ for calculating the results. But such a condition would seldom be found in natural waters.

The errors affecting the accuracy of Seyler's method are those which arise in part from the determination of the free CO_2. The end-point in the titration of the sample with sodium carbonate and phenolphthalein is not entirely satisfactory. The results obtained are usually low, but with care and practice the error from this source should be less than 2 to 3 parts per million, even with considerable amounts of CO_2, and on small amounts it is less still.

The error due to the determination of the fixed carbonic acid, from which the half-bound is derived, arises from those errors involved in the carrying out of Hehner's method which in good work ought not to exceed 1 to 2 parts per million.

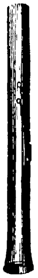

Fig. 31.

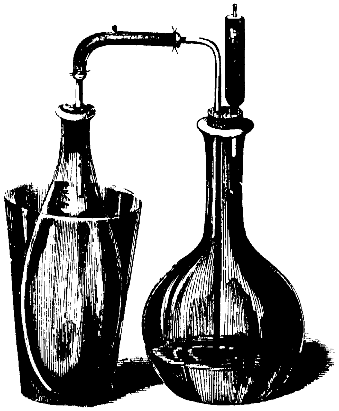

Fig. 32.

4. Carbonic Acid in Aerated Beverages, etc.

For determining the quantity of CO_2 in bottled aerated waters, such as soda, seltzer, potass, and others, the following apparatus is useful.

Fig. 31 is a brass tube made like a cork-borer, about five inches long, having four small holes, two on each side, and about two inches from its cutting end; the upper end is securely connected with the bent tube from the absorption flask (fig. 32), by means of a rubber tube; the flask contains a tolerable quantity of pure ammonia, into which the delivery tube dips; the tube *a* contains broken glass moistened with ammonia.

Everything being ready the brass tube is greased, and the bottle being held in the right hand, the tube is screwed a little aslant through the cork by turning the bottle round, until the holes appear below the cork and the gas escapes into the flask. When all visible action has ceased, after the bottle has been well shaken two or three times to evolve all the gas that can possibly be eliminated, the vessels are quietly disconnected, the tube *a* washed out into the flask, and the contents of the bottle added also; the whole is then precipitated with calcium chloride and boiled, and the precipitate titrated as usual. This gives the total CO_2 free and combined.

To find the quantity of the latter, another bottle of the same manufacture must be evaporated to dryness, and the residue gently ignited, then titrated with normal acid and alkali; the amount of CO_2 in the monocarbonate, deducted from the total, will give the weight of free gas originally present.

The volume may be found as follows:—1000 c.c. of CO_2 at 0°, and 760 mm. weigh 1·9769 gm. (Rayleigh). Suppose, therefore, that the total weight of CO_2 found in a bottle of ordinary soda water was 2·8 gm., and the weight combined with alkali 0·42 gm., this leaves 2·38 gm CO_2 in a free state—

$$1{\cdot}9769 : 2{\cdot}38 :: 1000 : x = 1204 \text{ c.c.}$$

If the number of c.c. of carbonic acid found is divided by the number of c.c. of soda water contained in the bottle examined, the quotient will be the volume of gas compared with that of the soda water. The volume of the contents of the bottle is ascertained by marking the height of the fluid previous to making the experiment; the bottle is afterwards filled to the same mark with water, emptied into a graduated cylinder and measured; say, the volume was 292 c.c., therefore

$$\frac{1204}{292} = 1{\cdot}12 \text{ vols. } CO_2.$$

5. Carbonic Acid in Air.

A dry glass globe or bottle capable of being securely closed by a rubber stopper, and holding 4 to 6 litres, is filled with the air to be tested by means of a bellows aspirator; baryta or lime water, containing a little barium chloride, is then introduced in convenient quantity and of known strength as compared with $^N/_{100}$ acid. The vessel is securely closed, and the liquid allowed to flow round the sides at intervals during half an hour or more. When absorption is judged to be complete, the alkaline solution is emptied out quickly into a stoppered bottle, and the excess at once ascertained in a measured portion by $^N/_{100}$ oxalic or hydrochloric acid and turmeric paper as described on p. 55. The final calculation is, of course, made on the total alkali originally used, and upon the exact measurement of the air-collecting vessel.

It is above all things necessary to prevent the absorption of CO_2 from extraneous sources during the experiment, especially from the breath of the operator. The error may be reduced to a minimum by carrying on the titration in the vessel itself, which is done by fixing an accurately graduated pipette through the cork or rubber stopper of the air vessel, to the upper end of which is attached a stout piece of elastic tube, closed with a pinch-cock; and this being filled to the 0 mark with dilute standard acid acts as a burette. The baryta or lime solution tinted with phenolphthalein is placed in the air bottle, which must be of colourless glass, and after the absorption of all CO_2 the excess of alkali is found by running in the acid until the colour disappears.[1]

The cork or stopper must have a second opening to act as ventilator; a small piece of glass tube does very well.

If a freshly made solution of oxalic acid is used containing 2·8636 gm. per litre, each c.c. represents 1 mgm. CO_2. The liquid holds its strength correctly for a day, and can be made as required from a strong solution, say 28·636 per litre.

Another method of calculation is to convert the volume of baryta solution decomposed into its equivalent volume in $^N/_{10}$ acid, 1 c.c. of which = 0·0022 gm CO_2 or by measurement at 0° C. and 760 mm. pressure represents 1·119 c.c. The method above described is a combination of those of Pettenkofer and Dalton, and, though much used, is liable to considerable error from various causes.

These errors have been examined by Letts and Blake,[2] more especially as to absorbing the CO_2 by baryta from a sample of air collected in a glass vessel and titrating with acid, and they show that, in addition to the more obvious sources of error, the action of the alkaline absorbent on the glass is one of importance.

In order to avoid it, they coated both the receiver containing the air sample and the bottle holding the stock of standard solution of baryta with paraffin wax. By this means they at once obtained more concordant results in a series of determinations. They then proceeded to test the degree, both of accuracy and of delicacy, of Pettenkofer's process if carried out with all the available precautions which suggested themselves. For this purpose they employed paraffined receiving vessels, an apparatus for performing the titrations in a vacuum, and burettes of special construction. In addition, an apparatus was used for delivering very accurately measured volumes of pure carbonic anhydride into known volumes of air previously freed from that gas.

Experimenting with such mixtures of the two as occur in air containing about 3 vols. of CO_2 in 10,000, the authors show that with careful work the mean error in the determinations need not exceed 0·04 part. The actual quantity of CO_2 added to each receiver full of air, in a series of five experiments, amounted to 0·927 c.c., and the mean amount found to 0·916 c.c., giving, therefore, a mean error of—0·011 c.c.

They thus show that Pettenkofer's process, if properly performed, is one of great accuracy and delicacy.

A. H. Gill in a report from the Sanitary and Gas Analysis Laboratory of the Technical Institute at Boston, U.S.A.,[3] gives a somewhat modified arrangement of the Pettenkofer method. Ordinary green glass bottles of one or two gallons capacity are measured by filling them with water, and the contents in c.c. ascertained, preferably by weighing on a good balance.

---

[1] Some operators prefer a standard mixture of caustic soda or potash containing some barium chloride to the baryta or lime solution. This is adopted by Symons and Stephens with acetic acid as control. The method used by them, which gives excellent results, is explained in their voluminous paper contributed to *J.C.S. Trans.*, 1896, pp. 869-881.

[2] *Proc. Chem. Soc.*, 1896, 192.

[3] *Analyst*, 1892, 17, 184.

The bottles are dried before being used. This may easily be done by rinsing first with alcohol or methylated spirit, draining, then rinsing with ether, and after again draining the bottle is quickly dried by blowing air through it with the ordinary laboratory bellows. If this plan is not used they must be dried, after draining well, in a warm place. A special form of bellows for filling the bottle with air is used by Gill, but the usual aspirator made on the accordion pattern suffices, or a small fan blower, the driving parts of which are connected by rubber bands to render it noiseless, may be used.

The bottle is fitted with a rubber stopper carrying a glass tube, closed by a plug of solid rubber.

The air to be tested is drawn into the bottle by repeated use of the aspirator so as to collect a representative sample, and if the test is made in a room everything should be quiet, and care must be taken to avoid draughts or the proximity of a number of persons.

METHOD OF PROCEDURE. 50 c.c. of the standard barium hydrate are rapidly run into the bottle from a burette (the jet passing entirely through the tube in the stopper), the cap replaced, and the solution spread completely over the sides of the bottle while waiting three minutes for the draining of the burette, before reading, unless it be graduated to deliver 50 c.c. The bottle is now placed upon its side, and shaken at intervals for forty to sixty minutes, taking care that the whole surface of the bottle is moistened with the solution each time. The absorption of the last traces of CO_2 is very slow indeed, half an hour in many cases being insufficient.

At the time at which the barium solution is added the temperature and pressure should be noted. At the end of the above period, shake well to ensure homogeneity of the solution, remove the cap from the tube, and invert the large bottle quickly over a 60 or 70 c.c. glass stoppered bottle, so that the solution shall come in contact with the air as little as possible. Without waiting for the bottle to drain, withdraw a portion of 15 or 25 c.c. with a narrow-stemmed spherical-bulbed pipette and titrate with sulphuric acid[1] (1 c.c. = 1 mgm. CO_2), using rosolic acid as an indicator. The difference between the number of c.c. of standard acid required to neutralize the amount of barium hydrate (e.g, 50 c.c.) before and after absorption gives the number of miligrams of CO_2 present in the bottle.

This is expressed in cubic centimetres under standard conditions, and divided by the capacity of the bottle under standard conditions, and the results reported in parts per 10,000. To reduce the air in the bottle to standard conditions, a hygrometric measurement of the air in the room from which the sample was taken is necessary. This in ordinary cases is usually omitted, as the object of the investigation is

---

[1] Sulphuric acid, in distinction from oxalic acid, enables one to determine the excess of barium hydrate in presence of the suspended barium carbonate, and also of caustic alkali, which is a frequent impurity of commercial barium hydrate. Professor Johnson, in the American edition of Fresenius's *Quantitative Analysis*, calls attention to the fact that the normal alkali oxalates decompose the alkaline earthy carbonates, so that the reaction continues alkaline if the least trace of soda or potash be present. The sulphuric acid may be prepared by diluting 46·51 c c. normal sulphuric acid to a litre.

comparative results, as regards the efficiency of ventilation, and the rooms in the same building would not vary appreciably in the amount of moisture in the atmosphere. This correction may make a difference of about 0 15 parts per 10,000.

Another method on the same principle is to attach a bulb apparatus, containing a measured quantity of baryta or lime water, to an aspirator bottle filled with water ; the tap of the bottle is opened to such an extent as to allow the air to bubble through the test solution at a moderate rate. The process of titration is the same as that given above. This method takes longer time, and the volume of air, which should not be less than five or six litres, is ascertained by measuring the volume of water allowed to run out of the aspirator, the rate of flow being regulated so that from two to three hours are required to pass the above volume of air. If a flask, fitted with tubes, is used in place of the bulb apparatus, the titration may be done without transferring the test solution.

6. Scheibler's Calcimeter for the determination of Carbonic Acid by Volume.

This apparatus is adapted for the determination of the CO_2 contained in native carbonates, as well as in artificial products, and has been specially contrived for the purpose of readily determining the CO_2 in the bone-black used in sugar refining. The principle upon which the apparatus is founded is simply this :—That the quantity of CO_2 contained in calcium carbonate may be used as a measure of the quantity of that salt itself ; and instead of determining, as has usually been the case, the quantity of gas by weight, this apparatus admits of its determination by volume ; and it is by this means possible to perform, in a few minutes, operations which would otherwise take hours to accomplish, while, moreover, the operator need possess scarcely any knowledge of chemistry. The results obtained by this apparatus are said to be correct enough for technical purposes.

The apparatus is shown in fig. 33, and consists of the following parts :—

The glass vessel, A, serves for the decomposition of the material to be tested for CO_2 which for that purpose is treated with dilute HCl ; this acid is contained, previous to the experiment, in the gutta percha vessel s. The glass stopper of A is perforated, and through it firmly passes a glass tube, to which is fastened the india-rubber tube r, by means of which communication is opened with B, a bottle having three openings in its neck. The central opening of this bottle contains a glass tube (r) firmly fixed, which is in communication, on the one hand, with A, by means of the flexible india-rubber tube already alluded to, and, on the other hand, *inside* of B, with a very thin india-rubber bladder, K. The neck (q) of the vessel B is shut off during the experiment by means of a piece of india-rubber tubing, kept firmly closed with a spring clamp. The only use of this opening of the bottle B, arranged as described, is to give access of atmospheric air to the interior of the bottle, if required. The other opening is in communication with the measuring apparatus C, a very accurate cylindrical glass tube of 150 c.c. capacity, divided into 0·5 c.c. ; the lower portion of this tube C is in communication with the tube D, serving the purpose of controlling the pressure of the gas. The lower part of this tube D ends in a glass tube of smaller diameter, to which is fastened the india-rubber tube *p*, leading to E, but the communication between these parts of the apparatus is closed, as seen at *p*, by means of a spring clamp. E is a water reservoir, and on removal of the clamp at *p*, the water contained in C and D runs off towards E; when it is desired to force the water contained in E into C and D, this can be readily done by blowing with the mouth into V, and opening the clamp at *p*.

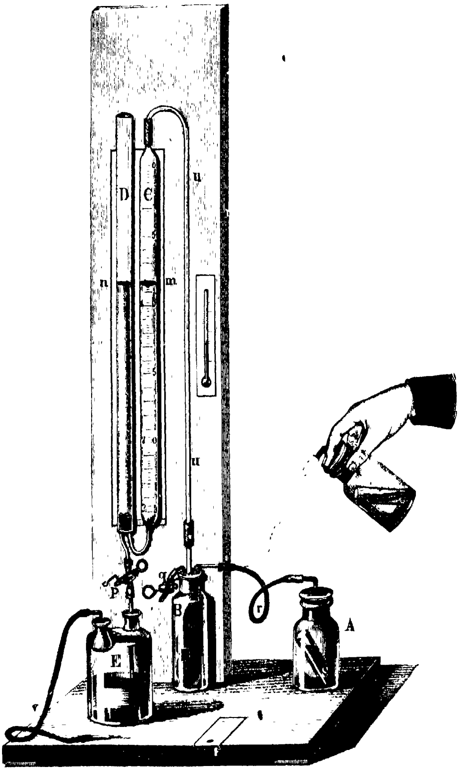

Fig. 33.

Precise directions for the use of this instrument are issued by the makers and need not be repeated here. It has been considerably used for technical purposes, but is liable to serious errors, for which various corrections have to be made, but even then there is room for considerable improvement.

This improvement has been made by A. Marshall,[1] and the apparatus is shown in fig. 34.

It consists of a gas reduction tube M, and a measuring tube E, which both pass through corks to the bottom of the Woulfe's bottle H, which is so fitted that the pressure of air in it can be accurately adjusted. It contains some refined petroleum oil of high boiling point, which can be forced into the tubes M and E. M contains such a quantity of air that, if it were reduced to 0° C. and 760 mm. pressure, it would just fill the tube down to a certain mark on it. The tube E is graduated in cubic centimetres, and is fitted at the top with a three-way cock of special design, by means of which it can be brought into communication either with the atmosphere or with the tube G, which leads to the generating vessel A. Branching out of G is the mercury manometer D, which enables one to adjust the pressure inside A, G, and E till it is equal to the atmospheric pressure. The generating vessel A is fitted with a well-ground tubulated stopper, and contains a small glass tube B to hold the acid. It is inserted in the glass water-bath C, which should contain cold water.

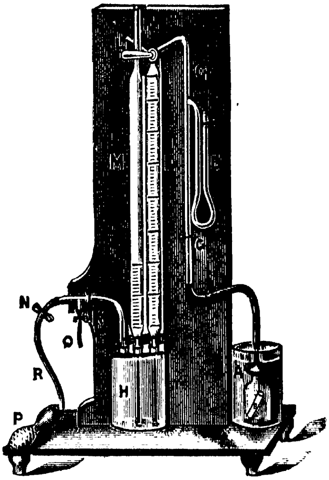

Fig. 34.

Briefly stated, a determination is conducted as follows:—The carbon dioxide is generated by the action of a small volume, 1 c.c., of concentrated hydrochloric acid on a weighed quantity of the substances to be tested; 0·1 to 0·8 or more gm. should be taken, according to the percentage of carbonic acid it contains. A mixture of air and carbon dioxide passes over into the measuring tube E. When the action is complete, the pressure is adjusted, till the manometer D shows that it is equal to that of the atmosphere. The cock is then turned off, and the pressure is again adjusted till the liquid in M stands at the highest graduation. The volume in E is then read off. This, without any correction whatever, is the volume of carbon dioxide contained in the substance taken. The whole operation does not take more than ten to fifteen minutes.

---

[1] *J. S. C. I.*, 1898, 17, 1106.

The gas reduction tube E acts on the same principle as that in Lunge's well-known "gas volumeter". To give absolutely accurate results the level of liquid in M and E should be the same. The density of the petroleum is, however, so small that the error from this cause never amounts to more than 0·3 c.c. with an apparatus having the dimensions selected by the inventor.

Carbon dioxide is slightly soluble even in heavy petroleum oil, but the solution proceeds very slowly. In the case of this apparatus, if the printed instructions be followed, only a dilute mixture of carbon dioxide can come in contact with the petroleum. The error due to this cause therefore falls well within the limits of experimental error due to other causes.

The error due to the solubility of carbon dioxide in hydrochloric acid is reduced to a minimum by employing a small quantity of concentrated acid; using 1 c.c. of acid of 1·17 sp. gr. it does not amount to more than 0·5 c.c. This error is in the opposite direction to that due to the inequality of the levels in the tubes M and E. Consequently it is to a great extent neutralized by the latter. Concentrated hydrochloric acid dissolves less carbon dioxide than the same volume of dilute acid.

If the generating vessel A be not kept cool a notable quantity of hydrogen chloride is expelled from it, and is slowly reabsorbed as the apparatus cools down again. This, of course, would interfere with the accuracy of the process. During the action the vessel should, therefore, be kept immersed in cold water. The cold-water bath also tends to prevent the temperature of the generating apparatus varying to any perceptible extent. Any error due to the latter cause is, in addition, greatly reduced by the small volume of the generating apparatus, which is not more than 100 c.c.

The following are the chief advantages of the apparatus described :—

1. The quantity of carbon dioxide dissolved in the acid is reduced to a minimum by using a small quantity of concentrated acid.

2. No corrections have to be made for temperature and pressure; consequently no reading of thermometer or barometer need be taken.

3. The total volume of the generating and measuring apparatus being less than 100 c.c., and the generating vessel being immersed in a considerable quantity of cold water, the volume of the air inside it cannot change during a determination to an extent sufficient to introduce a perceptible error.

4. The apparatus is quite simple, and although no barometer or thermometer is required the results are considerably more accurate than those obtained with Scheibler's.

To determine the percentage of $CaCO_3$ in any substance, weigh out accurately 0·224 gm. and proceed as above. The volume found, multiplied by 2, gives the per cent. of $CaCO_3$.

CITRIC ACID.

$C_3H_4(OH)(COOH)_3, H_2O = 210·081.$

THIS acid in the free state may readily be titrated with normal soda and phenolphthalein. 1 c.c. normal alkali = 0·070027 gm. crystallized citric acid.

1. **Citrates of the Alkalis and Earths.**—These citrates may be treated with neutral solution of lead nitrate or acetate, in the absence of other acids precipitable by lead. The lead citrate is washed with a mixture

of equal parts alcohol and water, the precipitate suspended in water, and H_2S passed into it till all the lead is converted into sulphide; the clear liquid is then boiled to remove H_2S, and titrated with normal alkali.

Citrates of the alkalis are converted by ignition to carbonate, which may be titrated with standard acid. Two molecules of citrate yield three of carbonate. 1 c.c. $^{N}/_{1}$ acid = 0·108119 gm. $K_3C_6H_5O_7$, H_2O.

2 Fruit Juices, etc.—If tartaric is present, together with free citric acid, the former is first separated as potassium bitartrate, which can very well be done in the presence of citric acid.

Method of Procedure: A cold saturated solution of potassium acetate in proof spirit is added to a somewhat strong solution of the mixed acids in proof spirit in sufficient quantity to separate all the tartaric acid as bitartrate, the mixture after stirring well being allowed to stand some hours. The precipitate is then transferred to a filter, and washed with proof spirit, then rinsed off the filter with a cold saturated solution of potassium bitartrate, and allowed to stand some hours, with occasional stirring; this treatment removes any adhering citrate. The bitartrate is again brought on to a filter, washed once with proof spirit, then dissolved in hot water, and titrated with normal alkali, 1 c.c. of which = 0·15 gm tartaric acid.

The first filtrate may be titrated for the free citric acid present after evaporating the bulk of the alcohol.

3. Lime and Lemon Juices.—The citric acid contained in lemon, lime, and similar juices, may be very fairly determined by Warington's method.[1]

Method of Procedure. 15 or 20 c.c. of ordinary juice, or 3-4 c.c. of concentrated juice are first exactly neutralized with pure normal soda, made up, if necessary, to about 50 c.c., heated to boiling in a salt bath, and so much solution of calcium chloride added as to be slightly in excess of the organic acids present. The mixture is kept at the boiling point for about half an hour, the precipitate collected on a filter and washed with hot water, filtrate and washings concentrated to about 15 c.c., and a drop of ammonia added; this will produce a further precipitate, which is collected separately on a very small filter by help of the previous filtrate, then washed with a small quantity of hot water. Both filters, with their precipitates, are then dried, ignited at a low red heat, and the ash titrated with normal or $^{N}/_{10}$ acid, each c.c. of which represents respectively 0·07 or 0·007 gm. $H_3\overline{Ci}$, H_2O.

FORMIC ACID.

$HCOOH = 46·016.$

H. C. Jones[2] has worked out a method which though not acidimetric may be quoted here. It is based on a process originally devised by Péan de Saint-Gilles, viz. titration with permanganate in the presence of an alkali carbonate. Lieben[3] confirmed this, using a more elaborate process. The method is on the same principle, but the procedure differs from that of Lieben.

---

[1] *J. C. S.*, 1875, 934.

[2] *Amer. Chem. Jour.*, 1895, **17**, 539-541.

[3] *Monatsh.*, 1894, **14**, 746.

METHOD OF PROCEDURE · The solution containing the formic acid is made alkaline with Na_2CO_3, warmed, and an *excess* of standard permanganate added. All the formic acid is thus oxidized, and a precipitate of manganese hydroxide thrown down. The solution is acidified with H_2SO_4, and a measured volume of oxalic acid run in until all the precipitate has dissolved and the permanganate disappeared. The excess of oxalic acid is then titrated with standard permanganate. A volume of oxalic acid equal to that taken is also titrated with the permanganate solution, and the difference between the result and the total permanganate used gives the quantity of permanganate required to oxidize the formic acid. The experimental results agree well among themselves and with those obtained by other methods, but the method is unreliable in the presence of much chloride.

The author further shows that Saint-Gilles' statement that oxalic acid can be titrated in acid solution in the presence of formic acid is unreliable, since formic acid is also oxidized to some extent by the permanganate under these conditions.

In the mercuric chloride method of Auerbach and Pluddemann[1] the reducing action of formic acid is made use of :—

$$HCO_2H + 2HgCl_2 = Hg_2Cl_2 + 2HCl + CO_2.$$

The formic acid solution, after neutralization, is heated for two hours in a boiling water-bath with a known excess of standard mercuric chloride solution, sodium acetate being also added. After filtering off the precipitated mercurous chloride, and cooling, the excess of mercuric chloride is titrated with standard potassium iodide solution (*vide* under Mercury (4)). The mercuric solution should contain 58·87 gm. of the salt and 15 gm. sodium chloride per litre. H. Fincke[2] has investigated the determination of formic acid in foods by this method.

HYDROFLUORIC ACID, HYDROFLUOSILICIC (SILICOFLUORIC) ACID, AND FLUORIDES.

1 c.c. of $^N/_1$ alkali = 0·02 gm. of HF = 0·024 gm. of H_2SiF_6.

COMMERCIAL hydrofluoric acid is as a rule far from pure. It generally contains hydrofluosilicic acid, sulphuric acid, sulphurous acid, and frequently traces of iron and lead. Two analyses of commercial acid gave the following figures :—

	1	2
Hydrofluoric acid	48·00	45·80
Hydrofluosilicic acid	13·05	9·49
Sulphuric acid	4·07	3·23
Sulphurous acid	0·49	1·06
Left on evaporation	0·16	—
Water by difference	34·23	40·42
	100·00	100·00

---

[1] *Z. Untersuch. Nahr. Genussm.*, 1909, **17**, 425.

[2] *Z. Untersuch. Nahr. Genussm.*, 1911, **21**, 1 ; and *Analyst*, 1911, **36**, 103.

If it is desired to prepare pure acid, the best way is to add to the commercial acid peroxide of hydrogen till it ceases to decolorize iodine, and then potassic hydric fluoride sufficient to fix all the hydrofluosilicic and sulphuric acids. Re-distillation in a lead retort with a platinum condenser will then give perfectly pure acid.

The total amount of free acid may be determined with normal alkali (preferably potash), using phenolphthalein or litmus, the former being best. Methyl orange and lacmoid do not give good results. In the case of pure acid, each c.c. of $^{N}/_{1}$ alkali indicates 0·02 gm. of HF, and the reaction when phenolphthalein is employed is very sharp. When, however, commercial acid is thus titrated a difference is observed; the pink colour obtained on adding the alkali only endures for a second or so and then fades away, and this may be repeated for some time till at last a permanent pink is produced. The cause of this is the presence of hydrofluosilicic acid. The first appearance of pink ensues when the reaction $H_2SiF_6 + K_2O = K_2SiF_6 + H_2O$ occurs. Then another reaction sets in.

$$K_2SiF_6 + 2K_2O = 6KF + SiO_2,$$

but from the slight solubility of the potassium silicofluoride some time elapses before it is complete.

The sulphuric and sulphurous acids must also be determined if the real amount of HF is required.

Determination of Sulphuric Acid in Presence of Hydrofluoric Acid (W. B. Giles).—Long experience has convinced the author of this new process that all methods depending upon the supposed solubility of barium fluoride, and the corresponding insolubility of the sulphate, in either hot or cold diluted hydrochloric acid, give most erroneous results. For instance, a sample of hydrofluoric acid known to contain 4 per cent. of H_2SO_4 was treated in the way described by Fresenius, using a large volume of hot dilute hydrochloric acid, and the precipitate was copiously washed with the same weak acid. The barium precipitate obtained was equal to 6·08 per cent. of H_2SO_4 or over 50 per cent. more than was present, and it was found that on repeatedly moistening the precipitate with dilute H_2SO_4, and re-igniting, the weight increased materially, showing co-precipitation of barium fluoride. The author therefore devised the following process for the determination of the SO_3, which gives accurate results. Its basis is—

1. The conversion of HF into H_2SiF_6, which is easily accomplished.

2 The precipitation of the SO_3 from this solution by means of lead silicofluoride.

3. The total insolubility of $PbSO_4$ in a solution containing an excess of the said lead salt.

METHOD OF PROCEDURE: A convenient weight of the hydrofluoric acid is placed in a platinum dish, about half its volume of water is added, and then precipitated silica in evident excess, and the whole is allowed to stand with occasional stirring for a few hours. It is then filtered, using an ebonite funnel, into another suitable platinum basin, and the excess of silica thoroughly washed. The filtrate and washings are then evaporated to a convenient bulk, and solution of lead silicofluoride is added in excess. If the least trace of sulphuric acid was originally contained in the acid, an almost immediate precipitate of $PbSO_4$ will form, as it is exceedingly insoluble in the presence of the lead silicofluoride. The solution is allowed to stand an hour or two, and the $PbSO_4$ separated by filtration, when it can of course be treated in any convenient volumetric way for the determination of the lead, or it may be weighed direct.

Lead silicofluoride is easily prepared by saturating commercial HF with coarsely powdered flint in a lead basin, and then agitating with powdered litharge. Its solubility is very great, and the specific gravity of the solution may reach 2·000 or more.

EXAMPLE To 37·89 gm. of chemically pure HF of 1250 sp. gr. there was added 25 c.c. of normal acid (= 1·0 gm. SO_3). The mixture was then treated as described above, and gave $PbSO_4$ 3·782 gm. = 1·0002 gm. of SO_3.

Determination of the Hydrofluosilicic Acid. To a convenient quantity of the acid contained in a platinum dish a solution of potassium acetate in strong methylated spirit is added in excess, and then more spirit is added, so that there may be about equal volumes of liquid and spirit. Allow to stand for several hours, and then filter and wash with a mixture of half spirit and half water. The resulting potassium silicofluoride may then be titrated with normal alkali according to the equation:

$$K_2SiF_6 + 2K_2O = 6KF + SiO_2,$$

or if the filter was a weighed one, it may be dried at 100° C. and weighed direct.

EXAMPLE: 2 gm. of chemically pure precipitated silica were dissolved in a large excess of pure diluted HF. Treated as above described, it yielded 7·35 gm. of K_2SiF_8 which equals 2·004 gm. of silica. 2 gm. of some powdered flint treated in the same way with 50 gm. of pure HF (of 10 per cent.) gave 7·168 gm. of K_2SiF_6 = 1·958 gm of silica.

Sulphurous Acid.—This is easily determined by taking the solution which results from the total acidity determination and titrating with decinormal iodine. Commercial hydrofluoric acid generally contains from 0 5 to 2·0 per cent.

The amount of each of the impurities being thus known, the percentage of real HF is easily calculated; e.g. 10 gm. of an acid was found to neutralize 276·0 c.c. of normal alkali. It was found to give the following results -

c.c. normal alkali 8·0 = 3·23 SO_3
" " " 39·0 = 9·36 H_2SiF_6
276 - 47 = 229 c.c. × 0·02 = 45·80 per cent. HF.
41·61 per cent. H_2O by difference

100 00

In this instance the amount of SO_2 was not allowed for.

Bifluorides.—These salts may be titrated in the same way as the acid with phenolphthalein. They generally contain some silicofluoride.[1]

The determination of fluorine in soluble fluorides has been done volumetrically by Knobloch.[2] The process is based on the following facts:—

When a solution of ferric chloride is mixed with its equivalent quantity of potassium fluoride the decomposition is complete, and the resulting ferric fluoride solution is colourless. In this state the iron is not detectable by such tests as thiocyanate, salicylic acid, etc. Still more interesting is the fact that ferric fluoride does not liberate iodine from iodides.

---

[1] The whole of this section, to this point, has been kindly contributed by W. B. Giles, F.I.C., who has had large practical experience in the subjects treated.

[2] *Pharm. Zeitschrift*, **39**, 558.

The following standard solutions, etc., are required :—

N/10 potassium fluoride; 5·809 gm. of the pure ignited salt in a litre of water

N/60 solution of ferric chloride, which the author prepared by diluting 19 gm. of the officinal ferric chloride of the Prussian pharmacopœia to a litre.

N/30 sodium thiosulphate solution.

Zinc iodide solution, made by mixing 10 gm. of iodine, 5 gm. of zinc powder, and 25 c c. of water in a flask, and warming till the violent action is over and the solution colourless, then diluting to 40 c c. and filtering.

METHOD OF PROCEDURE The liquid containing the fluorides in solution is mixed with a known excess of ferric chloride solution, then with excess of zinc iodide, and allowed to remain in a closed vessel at 35-40° C. for half an hour; the liberated iodine is then titrated with thiosulphate. The volume of the latter used is deducted from that of the ferric chloride—the difference being the measure of the fluorine. 1 c.c. thiosulphate 0·0019 gm. F.

The author states that calcium and strontium in their soluble salts may also be determined by the same method by acidifying their solutions with hydrochloric acid, adding equal volumes, first of potassium fluoride and then of ferric chloride solution in excess, adding excess of zinc iodide, and digesting at 35-40° C. The liberated iodine is ascertained as before. 1 c.c. of thiosulphate 0·002 Ca.

None of these reactions have been verified by me, but the method as given here is novel, and probably capable of being developed with further experience.

A very interesting paper on the acidimetry of hydrofluoric acid is contributed by Haga and Osaka,[1] being the results of independent experiments made by them in the laboratory of the Imperial University, Japan.

The authors examined the behaviour of the usual indicators in the neutralization of hydrofluoric acid. That its alkali salts blue litmus and that its avidity number places it among the vegetable acids rather than with the strong mineral acids, appear to be the only two facts yet recorded bearing upon its acidimetry.

To get uniform indications it was found necessary to have not only the acid pure, but the titrating solutions also; a little silica, alumina, or carbon dioxide affecting the titration more than it would in the case of the ordinary mineral acids.

Phenolphthalein is the best indicator, and leaves nothing to be desired when potash or soda is used for the titration. Rosolic acid is almost equal to it, and can be used also with ammonia. With both indicators the change of colour has the advantage of being very evident in platinum vessels. Methyl orange is useless. Litmus, lacmoid and phenacetolin are all capable of being made to yield accurate results in the hands of an experienced operator.

---

[1] *J. C. S.*, 17, 18, 251.

The fact that accurate results can only be obtained with very pure acids and reagents militates against the value of any acidimetric process, and therefore the indirect method by Giles, described above, is of greater technical value.

OXALIC ACID.

$H_2C_2O_4, 2H_2O = 126{\cdot}048.$

The free acid can be accurately titrated with normal alkali and phenolphthalein.

Procedure when in combination with alkalis: The acid can be precipitated with calcium chloride as calcium oxalate, where no other matters precipitable by calcium are present. If acetic acid is present in slight excess it is of no consequence, as it prevents the precipitation of small quantities of sulphates. The precipitate is well washed, dried, ignited, and the carbonate titrated with normal acid, 1 c.c. of which = 0·063024 gm. cryst. oxalic acid.

Acid oxalates are titrated direct for the amount of free acid. The reaction continues to be acid until alkali is added in such proportion that 1 molecule acid = 2 atoms alkali metal.

The combined acid may be found by igniting the salt, and titrating the residual alkaline carbonate as above.

For determination by permanganate, see pp. 128 and 130.

PHOSPHORIC ACID.

$P_2O_5 = 142{\cdot}08.$

Thomson has shown in his researches on the indicators that phosphoric acid, either in the free state or in combination with soda or potash, may with very fair accuracy be determined by the help of methyl orange or phenolphthalein. If, for instance, normal potash be added to a solution of phosphoric acid until the pink colour of methyl orange is discharged, KH_2PO_4 is formed (112 KHO = 142 P_2O_5). If now phenolphthalein is added, and the addition of potash continued until a red colour appears, K_2HPO_4 is formed. (Again 112 KHO = 142 P_2O_5.) On adding standard hydrochloric or sulphuric acid until the pink colour of methyl orange reappears, the titration with standard potash may be repeated. In each case 1 c.c. normal potash = ·071 gm. P_2O_5 or ·098 gm. H_3PO_4, each titration acting as a check upon the others.

Or the titration may be made with phenolphthalein only. But to obtain a sharp end-reaction[1] the standard alkali must be free from carbonate and the solution should be cold and concentrated (preferably with the addition of sodium chloride, in order to prevent hydrolysis of the dibasic salt formed, whereby it tends to react alkaline to the indicator). $H_3PO_4 + 2KOH = K_2HPO_4 + 2H_2O$. 1 c.c. normal alkali = ·0355 gm. P_2O_5 or ·049 gm. H_3PO_4.

Many attempts have been made to utilize these reactions for the accurate determination of P_2O_5 in manures, etc., but, so far as my experience goes, without adequate success.

---

[1] The maximum intensity of colour must be taken as the end-point.

Titration as Ammonio-magnesium Phosphate.—Stolba[1] adopts an alkalimetric method, which depends upon the fact that one molecule of the double salt requires two molecules of a mineral acid for saturation.

METHOD OF PROCEDURE: The precipitation is made with magnesia mixture, the precipitate well washed with ammonia, and the latter completely removed by washing with alcohol of 50 or 60 per cent. The precipitate is then dissolved in a measured excess of $^N/_{10}$ acid, methyl orange added, and the amount of acid required found by titration with $^N/_{10}$ alkali. Care must be taken that all free ammonia is removed from the filter and precipitate, and that the whole of the double salt is decomposed by the acid before titration, which may always be ensured by using a rather large excess and warming. The titration is carried out in the cold.

This method has given me very good results in comparison with the gravimetric method. The same method is applicable to the determination of arsenic acid, and also of magnesia.

1 c.c. of $^N/_{10}$ acid = 0·00355 gm. P_2O_5
" " = 0·00575 gm. As_2O_5
" " = 0·002 gm. MgO

The reaction in the case of phosphoric acid may be expressed as follows:—

$$Mg(NH_4)PO_4 + 2HCl = (NH_4)H_2PO_4 + MgCl_2.$$

Determination of Phosphoric Acid in its Pure Solutions.—R. Segalle[2] has investigated various methods for the above purpose with the following result:—

By far the most accurate results are obtained by Glucksmann's method. In this, the phosphoric acid is precipitated by an excess of magnesia mixture of known strength in free ammonia, the precipitate filtered off, and the free ammonia left in solution is titrated by standard acid. From the equation—

$$H_3PO_4 + MgSO_4 + 3NH_3 = MgNH_4PO_4 + (NH_4)_2SO_4$$

it will be seen that $H_3PO_4 = 3NH_3$.

The following modification is recommended as being more convenient and simple. To the phosphoric acid solution, contained in a graduated flask, an excess of standard ammonia (preferably normal) is added, followed by an excess of a saturated neutral solution of magnesium sulphate. The liquid is then diluted to the mark, well shaken, and filtered, and the residual ammonia titrated in an aliquot part of the filtrate. "Methyl red" (see p. 36) is especially suitable sa indicator in this process, as in ammonia titrations of all kinds.

On account of its simplicity, the modified method is well adapted for ascertaining the strength of the solutions of phosphoric acid employed in pharmacy.

J. M. Wilkie[3] has devised a method for the direct titration of free tri-basic phosphoric acid in the same manner as other acids. To the phosphoric acid solution is added silver nitrate and sodium acetate, and the liberated acetic acid is titrated with standard baryta in the presence of phenolphthalein.

---

[1] *Chem. Cent.*, 1866, 727, 728.

[2] *Z. a. C.*, **34**, 33-39.

[3] *J. S. C. I.*, 1909, **28**, 68

From the equation,

$$H_3PO_4 + 3AgNO_3 + 3CH_3COONa = Ag_3PO_4 + 3NaNO_3 + 3CH_3COOH$$

it is seen that $H_3PO_4 \quad 3CH_3COOH$.

Method of Procedure: A suitable amount of the free acid is diluted to about 50 c.c., excess of approximately decinormal silver nitrate is then added and finally a large excess of 3 per cent. sodium acetate. After adding a few drops of phenolphthalein, baryta is run in until a permanent pink coloration is developed.

$$1 \text{ c.c. } {}^{N}/_{10}\ Ba(OH)_2 = 0{\cdot}00327 \text{ gm. } H_3PO_4$$
$$= 0{\cdot}00237 \text{ gm. } P_2O_5.$$

Unless an excessive amount of silver is added the end point is sharp and easy of recognition, since the precipitated silver phosphate readily settles, leaving the supernatant liquid nearly clear. The method is also available for the mono- and di-alkali phosphates (ammonium if present must be removed by evaporation or boiling with standard alkali), but in the presence of alkali carbonate it is necessary also to determine the amount of silver actually precipitated as silver phosphate.[1] (See under Phosphoric Acid and Phosphates.)

For example, if a weight w of Na_2HPO_4 requires b c.c. ${}^{N}/_{10}$ $Ba(OH)_2$ and a c.c ${}^{N}/_{10}$ $AgNO_3$, we have

$$\text{Per cent. } Na_2CO_3 = \frac{(a - 3b)\ 0{\cdot}177}{w}$$

$$\text{Per cent. } Na_2HPO_4 = \frac{a \times 0{\cdot}473}{w}$$

or in terms of P_2O_5 and total Na_2O.

$$\text{Per cent. } P_2O_5 = \frac{a \times 0{\cdot}237}{w}$$

$$\text{Per cent. } Na_2O = \frac{(a - b)\ 0{\cdot}31}{w}$$

Precautions.—All water used must be free from CO_2. In the case of Na_2HPO_4 it is necessary to free from CO_2 by boiling with at least sufficient standard acid to convert to NaH_2PO_4, due allowance being made in the baryta titration. The silver nitrate should be tested for neutrality by treating with excess of sodium chloride and then adding phenolphthalein and one drop of ${}^{N}/_{10}$ NaOH. The sodium acetate likewise must be neutral and free from carbon dioxide. Alkali chloride if present has no effect in the baryta titration but must be allowed for in the silver-titration.

Other methods are described under Phosphoric Acid and Phosphates.

FUMING SULPHURIC ACID

(Oleum.)

Nordhausen Oil of Vitriol.

This consists of a mixture of SO_3 and H_2SO_4. When rich in SO_3 it exists in a solid form, and being very hygroscopic cannot be weighed in the ordinary manner. Accordingly, it is weighed either in glass bulbs or in a Lunge and Rey's glass-tap pipette. The bulbs used for this purpose are of about 2 cm. diameter, with two capillary tubes fused in. The acid, if solid, is first melted and when quite homogeneous is sucked up into the bulb by means of an india-rubber tube attached to one capillary tube, the other being dipped in the acid. About 3-5 gm. are taken and the bulb should be about half-filled. The wet tube is carefully cleaned outside, and one of the capillary ends is sealed. The bulb is then weighed, best by supporting it on a platinum crucible with two nicks, on which the ends of the bulb rest. In case of fracture, the acid runs into the crucible instead of on the balance. When weighed, put the bulb, open end downward, into a small conical flask, into the neck of which it fits exactly, and containing sufficient water to cover well the lower part of the tube. Break off the other point, allow the acid to run out, blow a few drops of water into the upper capillary, and finally rinse the whole bulb tube by repeated aspiration of water. Dilute the liquid to 500 c.c. and titrate 50 c.c. of it with $N/5$ sodium carbonate solution, using methyl orange as indicator. From the acidity thus found must be deducted that due to SO_2, which is determined by titrating another portion with $N/10$ iodine. For each c.c. of the latter 0·05 c.c. normal sodium carbonate is subtracted, since with methyl orange the colour changes when SO_2 has passed into $NaHSO_3$.

---

[1] *J. S. C. I.*, 1910, **29**, 794.

Let n = no. of c.c. of sodium carbonate used,
m = ,, ,, $N/10$ iodine solution required for the same quantity of acid,

the acidity due to $H_2SO_4 + SO_3$ is

$$(n - 0{\cdot}05\ m) \times 0{\cdot}040035 \text{ in terms of } SO_3.$$

To the SO_3 thus found add the SO_2 (calculated = 0·0032035 m) and assume the residue, in the absence of solid impurities, to be water. By multiplying this water by 4·443 we obtain the quantity of SO_3 combined with it to form H_2SO_4, and by deducting this from the total acidity that of the *free* SO_3.

TARTARIC ACID.

$C_4H_6O_6$ = 150·048 (Dibasic).

THE free acid may be readily titrated with normal alkali and phenolphthalein.

1 c.c. normal alkali = 0·075024 gm. tartaric acid.

The amount of tartaric acid existing in tartaric acid liquors is best determined by precipitation as potassium bitartrate; the same is also the case with crude argols, lees, etc. Manufacturers are indebted to Warington and Grosjean for most exhaustive papers on this subject, to which reference should be made by all who desire to study the nature and analysis of all commercial compounds of citric and tartaric acids.[1]

Without entering into the copious details and explanations given by these authorities, the methods may be summarized as follows:—

---

[1] Warington, *J. C. S.*, 1875, 925-991; Grosjean, *J. C. S.*, 1879, 341-356.

Commercial Tartrates.

In the case of good clean tartars, even though they may contain sulphates and carbonates, accurate results may be obtained by indirect methods.

(*a*) The very finely powdered sample is first titrated with normal alkali, and thus the amount of tartaric acid existing as bitartrate is found; another portion of the sample is then calcined at a moderate heat, and the ash titrated. By deducting from the volume of acid so used the volume used for bitartrate, the amount of base corresponding to neutral tartrates is obtained.

(*b*) The whole of the tartaric acid is exactly neutralized with caustic soda, evaporated to dryness, calcined, and the ash titrated with normal acid; the total tartaric acid is then calculated from the volume of standard acid used; any other organic acid present will naturally be included in this amount. In the case of fairly pure tartars, etc., this probable error may be disregarded.

METHOD OF PROCEDURE: 5 gm. of the finely powdered tartar are heated with a little water to dissolve any carbonates that may be present. If it is wished to guard against crystalline carbonates, 5 c.c. of standard HCl are added in the first instance, and the heating is conducted in a covered beaker. Standard alkali is next added to the extent of about three-fourths of the amount required by a good tartar of the kind examined, plus that equivalent to the acid used, and the whole is brought to boiling: when nearly cold, the titration is finished. From the amount of alkali consumed, minus that required by the HCl, the tartaric acid present as acid tartrate is calculated.

2 gm. of the powdered tartar are next weighed into a platinum crucible with a well-fitting lid; the crucible is placed over an argand burner; heat is applied, very gently at first, to dry the tartar, and then more strongly till inflammable gas ceases to be evolved. The heat should not rise above very low redness. The black ash is next removed with water to a beaker. If the tartar is known to be a good one, 20 c.c of standard H_2SO_4 are now run from a pipette into the beaker, a portion of the acid being used to rinse the crucible The contents of the beaker are now brought to boiling, filtered, and the free acid determined with standard alkali. As the charcoal on the filter under some circumstances retains a little acid, even when well washed, it is advisable when the titration is completed to transfer the filter and its contents to the neutralized fluid, and add a further amount of alkali if necessary. From the neutralizing power of a gram of burnt tartar is subtracted the acidity of a gram of unburnt tartar, both expressed in c.c. of standard alkali; the difference is the neutralizing power of the bases existing as neutral tartrates, and is then calculated into tartaric acid on this assumption.[1]

If the tartar is of low quality, 5 c.c. of solution of hydrogen peroxide (1 volume = 10 volumes O_2) are added to the black ash and water, and immediately afterwards the standard acid, the rest of the analysis proceeds as already described; the small acidity usually belonging to the peroxide solution must, however, be known and allowed for in the calculation. By the use of hydrogen peroxide the sulphides formed during ignition are reconverted into sulphates, and the error of excess which their presence would occasion is avoided.

The above method does not give the separate amounts of acid and neutral tartrates in the presenes of carbonates, but it gives the correct amount of tartaric acid; it is also correct in cases where free tartaric acid exists, so long as the final results show that some acid existed as neutral salt. Whenever this method shows that the acidity of the original substance is greater than the neutralizing power of the ash, it will be necessary to use the method *b*, which is the only one capable of giving good results when the sample contains much free tartaric acid.

---

[1] It is obvious that the neutralizing power of the ash of an acid tartrate is exactly the same as the acidity of the same tartrate before burning. In making the calculations, it must be remembered that the value of the alkali in tartaric acid is twice as great in the calculation made from the acidity of the unburnt tartar as in the calculation of the acid existing as neutral tartrates.

Methods adopted by the Seventh International Congress of Applied Chemistry, London 1909.[1]

The crude tartrate should be carefully sampled, ground and passed through a sieve having a mesh of 0·5 mm.

Determination of the Bitartrate.—A weighed portion of 2·35 gm. of the sample is boiled for 5 minutes with 400 c.c. of water in a 500 c.c. flask, then cooled, diluted to the mark, mixed and filtered; 250 c.c. of the filtrate are heated to boiling, and titrated with $^N/_4$ potassium hydroxide solution, using litmus paper as indicator. The potassium hydroxide solution is standardized under the same conditions with pure potassium bitartrate.

Determination of total tartaric acid.—In cases of tartrates containing upwards of 45 per cent. of total tartaric acid, 6 gm. of the sample are taken for the determination, where the tartaric acid falls below 45 per cent., 12 gm. of the sample are used, this quantity being also taken for the analysis of calcium tartrates. The weighed portion of the sample is thoroughly mixed with 18 c.c. of hydrochloric acid of sp. gr. 1·1; after the lapse of 15 minutes, the mixture is rinsed into a 200 c.c. flask with water and diluted to the mark. The solution is then poured through a filter, 100 c.c. of the filtrate are heated to boiling and 10 c.c. of 66 per cent. potassium carbonate solution are added slowly. The mixture is heated for about 20 minutes and the liquid together with the precipitate is transferred to a 200 c.c. flask, cooled, and diluted to volume. After filtering, 100 c.c. of the filtrate are evaporated to a volume of 15 c.c., 3·5 c.c. of glacial acetic acid are added, drop by drop, and the mixture is stirred for 5 minutes; at the end of 10 minutes, 100 c.c. of 95 per cent. alcohol are added, the stirring is continued for 5 minutes, and, after the lapse of a further 10 minutes, the liquid portion is poured through a filter, the precipitate is washed three or four times by decantation with a little alcohol, then brought on to the filter and washed with alcohol until the washings are free from acidity. The filter together with the precipitate is then placed in a flask, boiled with 300 c.c. of water for 1 minute, and the hot solution titrated with $^N/_4$ potassium hydroxide solution, using litmus paper as indicator. The following corrections are made for the volume of the insoluble matter:—For tartrates containing 20 per cent. of total tartaric acid, 0·8 is deducted from the total percentage of acid found; for 30 per cent. tartrates, 0·70, and for 40 per cent. tartrates, 0·6. In the case of tartrates containing 50, 60, and 80 per cent. of tartaric acid, 0·25, 0·15, and 0·1 per cent. is deducted respectively.

Cream of Tartar.

When prepared by boiling crude tartar or "argol" with water, filtering, and crystallizing the salt from the clear liquid, cream of tartar always contains more or less calcium tartrate, which, though nearly insoluble in cold water, dissolves with moderate facility in a hot solution of acid tartrate of potassium. From experiments made, as well as from numerous analyses, Allen[1] concluded that the commercial article should not contain more than 9 or 10 per cent. of calcium tartrate. After a consideration of possible impurities, he recommended the following process:—

---

[1] P. Carles, *Ann. Chim. analyt.*, 1910, **15**, 231.

1. Dissolve 1·881 gm. of the moisture-free sample in hot water and titrate with $^{\mathrm{N}}/_{10}$ caustic alkali and phenolphthalein. In the absence of acid potassium sulphate (and of free tartaric acid) each c.c. of alkali required represents 1 per cent. of acid potassium tartrate in the sample.

2. Ignite 1·881 gm. of the moisture-free sample at a dull red heat for 10 minutes, without attempting to burn off all the carbon. Boil the product with water, filter, and wash the insoluble carbonaceous residue.

(*a*) Titrate the filtrate with $^{\mathrm{N}}/_{10}$ HCl and methyl-orange. In a pure sample the volume of acid required will exactly equal that of the alkali consumed in process 1. The presence of calcium tartrate in the sample does not affect the results. Each c.c. of *deficiency* of acid represents 0·36 per cent. of calcium sulphate ($CaSO_4$) or 0·72 per cent. of $KHSO_4$. Any *excess* of acid required points to the presence of neutral potassium tartrate, each c.c. of difference representing 0·60 per cent. of that salt.

(*b*) Ignite the carbonaceous residue, dissolve in 20 c.c. of $^{\mathrm{N}}/_{10}$ acid, filter if necessary, wash, and titrate the filtrate with $^{\mathrm{N}}/_{10}$ alkali and methyl-orange. Each c.c. required corresponds to 0·50 per cent. of calcium tartrate or 0·36 per cent. of $CaSO_4$.

---

[1] On the composition and analysis of commercial cream of tartar, *The Analyst*, 1896, **21**, 174 and 209

PART III.

ANALYSIS BY OXIDATION OR REDUCTION.

THE number of methods of analysis based on oxidation or reduction is very great, and not a few of them possess extreme accuracy, such accuracy, in fact, as it is not possible to attain by any gravimetric method. The completion of the various processes is generally shown by a distinct change of colour, e.g. the beautiful rose-red tint of permanganate and the blue colour of iodide of starch; and as the smallest quantity of these substances suffices to colour distinctly large volumes of liquid, the slightest excess of the oxidizing agent is sufficient to produce a distinct effect.

The principle involved in the process is extremely simple. Substances having a strong affinity for oxygen are brought into solution, and titrated with an oxidizing solution of known strength. For example, ferrous salts rapidly absorb oxygen, and when a solution of permanganate is gradually added to a solution of a ferrous salt the latter instantly discharges the colour of the drops at first run in, but after the whole of the ferrous salt has been converted into the ferric state the liquid becomes rose-coloured on the further addition of a few drops of permanganate, the appearance of this colour indicating the completion of the change. The reaction is, in its simplest form, as follows:—

$$10FeO + K_2Mn_2O_8 = 5Fe_2O_3 + 2MnO + K_2O.$$

The titration is carried out in the presence of dilute sulphuric acid, and sulphates are formed. Similarly, oxalic acid, in the presence of sulphuric acid, is readily oxidized by permanganate, carbon dioxide being formed. The reaction is:—

$$5H_2C_2O_4 + K_2Mn_2O_8 + 3H_2SO_4 = 10CO_2 + 2MnSO_4 + K_2SO_4 + 8H_2O.$$

Here, again, the appearance of a rose tint in the solution shows that the oxidation is complete.

The strength of many oxidizing agents is determined by adding a known quantity of a reducing agent in excess, then ascertaining the amount of this excess by residual titration with a standard oxidizing solution. The strength of the reducing solution being known, the quantity required is a measure of the substance which has been reduced by it.

The *oxidizing agents* most frequently used are potassium permanganate, iodine, potassium dichromate, and potassium ferricyanide.

The *reducing agents* employed are sulphurous acid, sodium thiosulphate, oxalic acid, ferrous salts, arsenious oxide, stannous chloride, potassium ferrocyanide, zinc and magnesium. Titanium chloride, a very powerful reducing agent, will be referred to later.

The most commonly used combinations of the above are:—

1. Permanganate and ferrous salts: permanganate and oxalic acid. Both used in sulphuric acid solution, the appearance of a rose colour being the indicator.

2. *Potassium dichromate and ferrous salts, with potassium ferricyanide as external indicator.*

3. Iodine and sodium thiosulphate; iodine and sodium arsenite; with starch as indicator in each case.

PREPARATION OF STANDARD SOLUTIONS.

PERMANGANIC ACID AND FERROUS OXIDE.

1. Potassium Permanganate.

$K_2Mn_2O_8$ = 316·06. Decinormal Solution 3·161 gm. per litre.

1 c.c. = 0·0008 gram Oxygen.

THE solution of this salt is best prepared for analysis by dissolving the pure crystals in freshly-distilled water, and should be of such a strength that 17·9 c.c. will oxidize 1 decigram of iron. The solution is then decinormal. As distilled water always contains traces of organic matter, about 3·161 gm. of the pure dry salt should be dissolved in a litre of water, and the solution either boiled or a stream of air (filtered through cotton wool) passed through it for some time. If the solution be now stored in a dark place for several weeks, it will be found that very little, if any, change in strength occurs. If not treated as above when first made, the solution should be kept from 8 to 14 days before use. It should then be filtered through asbestos, and standardized by titration in one of the following ways:—

2. Titration of Permanganate.

(*a*) **With Sodium Oxalate.**—Experiments made under the direction of the U.S. Bureau of Standards to discover the best conditions for this standardization have resulted in the recommendation of the following method:—

0·25-0·3 gm. of the oxalate (which should be dried at 100° for a few hours before use) is dissolved in 200-250 c.c. of water at 80-90° C in a 400 c.c. beaker, 10 c.c. of sulphuric acid (1 : 1) are added, and the permanganate solution is then immediately run in, with constant and vigorous stirring with a small thermometer instead of a glass rod. Not more than 10-15 c.c. should be added per minute, and the last 0·5-1·0 c.c. must be added drop by drop. The excess of permanganate necessary to produce the final colour must be ascertained by a control test. The solution must not be below 60° C. when the final point is reached. Results are accurate to 0·1 per cent., probably to 0·05 per cent.

Since $2Na_2C_2O_4$ yield O_2, 134 gm. of oxalate correspond to 16 gm. of oxygen, or 6·7 gm. of oxalate to 0·8 gm. of oxygen, i.e. to 1 litre of $^N/_{10}$ permanganate. Hence 0·25 gm. of sodium oxalate requires 37·31 c.c. of $^N/_{10}$ permanganate.

(*b*) **With Metallic Iron.**—There is no difficulty in obtaining iron of 99·8 per cent. purity. It is sold in the form of thin wire, each piece of which should be drawn between two pieces of fine emery cloth and then wiped with a dry cloth before use; this treatment removes rust.

Method of Procedure: Fit a tight cork or rubber stopper, with bent delivery tube, into a flask holding about 300 c.c., and clamp it in a retort stand in an inclined position, the tube being so bent as to dip into a small beaker containing pure water. Fill the flask one-third with pure dilute sulphuric acid, and add a few grams of sodium carbonate in crystals; the CO_2 so produced will drive out the air. While this is being done weigh about 0·1 gram of the wire; put it quickly into the flask when the soda is dissolved, and apply a gentle heat till the iron is completely in solution; a few black specks of carbon are of no consequence. The flask is then rapidly cooled under a stream of cold water, diluted if necessary with some recently boiled and cooled water, and the permanganate run in cautiously from a tap burette, with constant shaking, until a faint rose-colour is permanent.

The decomposition which ensues from titrating ferrous oxide by permanganic acid may be represented as follows:—

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$

The weight of wire taken, multiplied by 0·998, will give the actual weight of pure iron upon which to calculate the strength of the permanganate.

The content of iron in iron wire used may be determined by means of a permanganate solution that has been standardized by sodium oxalate.

(*c*) **With Ferrous Ammonium Sulphate.** In order to ascertain the strength of the permanganate, it may be titrated with a weighed quantity of this substance instead of metallic iron.

This salt is a convenient one for titrating the permanganate, as it saves the time and trouble of dissolving the iron, and when perfectly pure it can be depended on without risk. To prepare it, 139 parts of the purest crystals of ferrous sulphate, and 66 parts of pure crystallized ammonium sulphate are separately dissolved in the least possible quantity of distilled water at about 40° C. (if the solutions are not perfectly clear they must be filtered); mix them at the same temperature in a porcelain dish, adding a few drops of pure sulphuric acid, and stir till cold. During the stirring the double salt will fall in a finely granulated form. Set aside for a few hours, then pour off the supernatant liquid, and empty the salt into a clean funnel plugged with a little cotton wool so that the mother-liquor may drain away; the salt may then be quickly and repeatedly pressed between fresh sheets of clean filtering paper. Lastly, place in a current of air to dry thoroughly, so that the small grains adhere no longer to each other, or to the paper in which they are contained, then preserve in a stoppered bottle for use. Only a few ounces should be made at a time, according to the directions above, as if large quantities are made it is difficult to dry the granular salt in purely ferrous state.

The formula of the salt is $Fe(NH_4)_2(SO_4)_2, 6H_2O = 392·14$. Conse quently it contains almost exactly one-seventh of its weight of iron 0·7023 gm. represents 0·1 gm. Fe, and this is a convenient quantity t weigh for the purpose of titrating the permanganate.

Method of Procedure: 0·7023 gm. being brought into dilute col solution in a flask or beaker, and 20 c.c. of dilute sulphuric acid (1 to 5 added (the titration of permanganate, or any other substance by it should always take place in the presence of free acid, and preferabl sulphuric), the permanganate is delivered from a burette with glass tap as before described, until a slight rose colour persists.

(*d*) **With Oxalic Acid.**—This is a very quick method of titrating perman ganate, if the exact value of the solution of pure oxalic acid is known. 10 c.c. o normal solution are brought into a flask with dilute sulphuric acid, as in the case of the iron salt, and considerably diluted with water, then warmed to about 60 C., and the permanganate added from the burette. The colour disappears slowl at first, but afterwards more rapidly, becoming first brown, then yellow, and s on to colourless. More care must be exercised in this case than in the titration with iron, as the action is not momentary. 100 c.c. should be required to be strictly decinormal. The chemical change which occurs is explained on p. 127.

3. Precautions in Titrating with Permanganate.

It must be borne in mind that free acid is always necessary in titrating a substance with permanganate, in order to keep the resulting manganous oxide in solution. Sulphuric acid in dilute solution has no prejudicial effect on the pure permanganate, even at a high temperature. With hydrochloric acid the solution to be titrated must be very dilute and at a low temperature, otherwise chlorine will be liberated and the analysis spoiled. This acid acts as a reducing agent on permanganate in concentrated solution, thus—

$$Mn_2O_7 + 14HCl = 7H_2O + 5Cl_2 + 2MnCl_2.$$

The irregularities due to this reaction may be entirely obviated by the addition of a few grams of manganous or ammonium sulphate before the titration, which must be performed *slowly*.

In spite of the manifest advantages of standard dichromate where there are reasons for titrating iron in hydrochloric acid solution, many attempts have been made to work out a method with permanganate which shall be accurate and reliable under practical conditions.[1] For details of some of these methods see under Iron.

Organic matter of any kind decomposes the permanganate, and the solution therefore cannot be filtered through paper, nor can it be used in a clip burette, because it is decomposed by the india-rubber tube. It may, however, be filtered through gun-cotton or glass-wool.

---

[1] Fresenius, *Z. A. C.*, 1862, 361; Zimmermann, *Annalen*, 1882, 305; Reinhardt, *Chem. Z.*, 1889, 323; Brandt, *Chem. Z.*, 1908, 812, etc.; Friend, *Chem. Soc. Trans.*, 1909, **95**, 1228; Jones and Jeffery, *Analyst*, 1909, **34**, 306.

TITRATION OF FERRIC SALTS BY PERMANGANATE.

ALL ferric compounds requiring to be determined by permanganate must, of course, be reduced to the ferrous state. This is best accomplished by metallic zinc or magnesium in sulphuric acid solution. Hydrochloric acid may also be used with the precautions mentioned.

The reduction occurs on simply adding to the warm diluted solution small pieces of zinc (free from iron, or at least with a known quantity present) or coarsely powdered magnesium until colourless; or until a drop of the solution brought in contact with a drop of potassium thiocyanate produces no red colour. All the zinc or magnesium must be dissolved previous to the titration.

The reduction may be hastened considerably as shown under Iron 2. When the reduction is complete, no time should be lost in titrating the solution.

CALCULATION OF THE RESULTS OF ANALYSES MADE WITH PERMANGANATE SOLUTION.

THE calculation of the results of analyses with permanganate, if the solution is not strictly decinormal, may be made by ascertaining its coefficient, reducing the number of c.c. used for it to decinormal strength, and multiplying the number of c.c. thus found by $\frac{1}{10000}$ of the equivalent weight of the substance sought; for instance—

Suppose that 15 c.c. of permanganate solution have been found to equal 0·1 gm. iron; it is required to reduce the 15 c.c. to decinormal strength, which would require 1000 c.c. of permanganate to every 5·584 gm. of iron, therefore $5{\cdot}584 : 1000 :: 0{\cdot}1 : x = 17{\cdot}9$ c.c.; $17{\cdot}9 \times 0{\cdot}005584 = 0{\cdot}09995$ gm. iron, which is as near to 0·1 gm. as can be required. Or the coefficient necessary to reduce the number of c.c. used may be found as follows: $0{\cdot}1 : 15 :: 5{\cdot}584 : x = 83{\cdot}8$ c.c., therefore $\frac{100}{83{\cdot}8} = 1{\cdot}194$. Consequently 1·194 is the coefficient by which to convert the number of c.c. of that special permanganate to decinormal strength, whence the weight of substance sought may be found in the usual way.

Another plan is to find the quantity of iron or oxalic acid represented by the permanganate used in any given analysis, and this being done the following simple equation gives the required result :—

$$\begin{array}{ccccccc} \text{Fe (55·84)} & & \text{eq. weight of} & & \text{the weight} & & \text{the weight of} \\ \text{or} & : & \text{the substance} & :: & \text{of Fe or} & : & \text{substance} \\ \text{O (63·024)} & & \text{sought} & & \text{O found} & & \text{sought.} \end{array}$$

In other words, if the equivalent weight of the substance analysed be divided by 55·84 or 63·024 (the respective equivalent weights of iron or oxalic acid), a coefficient is obtained by which to multiply the weight of iron or oxalic acid equal to the permanganate used, and the product is the weight of the substance titrated.

For example: sulphuretted hydrogen is the substance sought, the eq. weight of H_2S corresponding to 2 eq. Fe is 17·043; let this number be divided by 55·84; $\frac{17·043}{55·84} = 0·3052$; therefore, if the quantity of iron represented by the permanganate used in a determination of H_2S be multiplied by 0·3052, the product will be the weight of the sulphuretted hydrogen sought.

Again: in the case of manganese peroxide, of which the equivalent weight is 43·465;

$$\frac{43·465}{55·84} = 0·7784.$$

The weight of iron, therefore, found by permanganate in any analysis multiplied by the coefficient 0·7784 will give the amount of peroxide MnO_2. Again: if m gm. iron = k c.c. permanganate, then 1 c.c. permanganate = $\frac{m}{k}$ gm. metallic iron.

The equivalents here given are on the hydrogen scale, in accordance with the normal system of solutions adopted; and thus it is seen that two equivalents of iron are converted from the ferrous to the ferric state by the same quantity of oxygen as suffices to oxidise one equivalent of oxalic acid, sulphuretted hydrogen, or manganese peroxide.

1 c.c. decinormal permanganate is equivalent to
0·005581 gm. Fe determined in the ferrous state
0·007184 ,, FeO ,, ,, ,,
0·008 ,, Fe_2O_3 ,, ,, ,,
0·003733 ,, Fe ,, from FeS
0·005935 ,, Sn ,, ,, $SnCl_2$
0·00298 ,, Sn ,, ,, SnS_2
0·00318 ,, Cu determined from CuS
0·00275 ,, Mn ,, ,, MnS
0·00318 ,, Cu ,, ,, $Cu + Fe_2Cl_6$
0·00636 ,, Cu ,, ,, CuO + Fe
0·001705 ,, H_2S
0·0008 ,, O
0·0063 ,, O
0·002 ,, Ca from CaC_2O_4
0·0120 ,, Ur ,, UrO, etc., etc.

When possible, the necessary coefficients will be given in the tables preceding any leading substance.

DETERMINATION OF FERROUS OXIDE BY POTASSIUM DICHROMATE.

(Penny's Method.)

POTASSIUM dichromate, as a reagent for the determination of ferrous iron, possesses the advantages over permanganate that it may easily be obtained in the purest state, it is absolutely permanent in solution, and its solution may be used in a Mohr's burette. On the other hand, the end of the reaction can only be ascertained by means of an external indicator. For this purpose a *freshly-made* and very dilute solution of potassium ferricyanide[1] is spotted on a white tile and drops of the ferrous solution are from time to time brought into contact with the spots of the indicator. At first a deep-blue colour is produced where the drops meet, but as the addition of dichromate is continued this gives place to a bluish green, then green, shade, and the titration is completed when a drop of the iron solution placed on the tile appears of the same colour as that of the mixed drops of solution and ferricyanide.

The reaction may be simply expressed as follows :—

$$2CrO_3 + 6FeO = Cr_2O_3 + 3Fe_2O_3.$$

The decomposition takes place immediately, and at ordinary temperatures, in the presence of free hydrochloric or sulphuric acid. Nitric acid is, of course, inadmissible.

The reduction of ferric compounds to the ferrous state may be effected by stannous chloride, sodium sulphite, ammonium bisulphite, sulphurous acid, or magnesium. Zinc is not so good for this purpose, as the zinc ferricyanide somewhat obscures the end-reaction. In the analysis of iron ores stannous chloride is most useful, as it very rapidly reduces the ferric salt and causes the yellow colour to disappear almost immediately. The reduction is carried out as follows :

The hydrochloric acid solution of iron, containing a large excess of free acid, is heated to boiling in a flask and fairly strong stannous chloride solution dropped into it from a burette[2] or a dropping tube till the yellow colour of the solution has nearly gone. The reduction is then finished by adding a more dilute solution of stannous chloride a drop at a time, with agitation after each addition, till the liquid has a faint sea-green colour, quite free from any tinge of yellow. To guard against any excess of stannous chloride that might be present and so lead to an unduly high result, about 4 c.c. of a 5 per cent. solution of mercuric chloride may be added : this converts any stannous chloride into the stannic compound with precipitation of mercurous chloride, which does not interfere with the titration. The flask is then emptied into a basin, rinsed out thoroughly with hot water, and the titration immediately proceeded with.

Reduction with sulphurous acid is carried out as follows : Rinse down the inside of the flask and slowly add dilute ammonia solution, constantly shaking the flask round, till a faint permanent precipitate is obtained. Next pour round the inside of the flask 25 c.c. of strong solution of SO_2 and then 50 c.c. of water, and boil till free from every trace of SO_2. The liquid should be quite free from any tinge of yellow. Then add to the solution 10 c.c. of dilute sulphuric acid (1 : 6) and titrate at once with dichromate solution.

For the analysis of iron ores it is most convenient to take 0·5 gm. for the analysis, and to use a solution of dichromate containing exactly 4·390 gm. of the pure crystals per litre. 1 c.c. = 0·005 gm. Fe, and the number of c.c. used in each determination gives the percentage of iron present without any calculation.[1]

---

[1] 0·03 gm. of the crystals dissolved in 20 c.c. of water.

[2] It is best to keep one for the purpose, as the solution gradually marks the glass.

1. Preparation of the Decinormal Solution of Potassium Dichromate.

4·903 gm. per litre.

From the equation

$$6FeO + K_2Cr_2O_7 = 3Fe_2O_3 + Cr_2O_3 + K_2O$$

we see that each molecule of potassium dichromate gives up 3 atoms of oxygen, equivalent to 6 atoms of hydrogen. Hence, as the molecular weight is 294·2, one-sixth of this in grams is equivalent to 1·008 gm. of hydrogen. In other words, a normal solution contains 49·033 gm. per litre. For most purposes, however, a decinormal solution, containing 4·903 gm. per litre, is more useful and is the one generally employed.

1 c.c. = 0·005584 gm. Fe.

2. Solution of Stannous Chloride.

10-15 gm. of pure tin are melted in a porcelain dish and poured from a height into cold water in a large porcelain dish. The granulated tin so obtained is transferred to a 300 c.c. flask and about 200 c.c. pure hydrochloric acid added, together with a piece of platinum foil The flask is covered with a glass marble or watch glass and heated on a hot plate till solution has taken place. The strong acid solution thus obtained is kept in a bottle with a rubber stopper, a few pieces of granulated tin being added in order to preserve the solution in the stannous state. For reduction of ferric salts about 5 c.c. of the solution is diluted to 100 c.c. with water when required.

IODIMETRY AND IODIMETRIC PROCESSES.

Iodimetry, or the process of determining iodine volumetrically, is based on a method, due to Dupasquier, of determining sulphurous acid by titration with a standard solution of iodine in potassium iodide, which was run into the sulphurous acid until a colour appeared. The reaction is according to the following equation:—

$$SO_2 + I_2 + 2H_2O = 2HI + H_2SO_4.$$

Incorrect results having frequently been obtained by this method, however, Bunsen investigated it and found the cause of failure to have been the use of a too concentrated solution of SO_2. He proved that the above equation held good only when sulphurous acid of no greater strength than 0·04 per cent. was used. With stronger solutions the action in a short time is reversed. By the use of a dilute solution of SO_2 standardized with an iodine solution of known value the strength of another iodine solution could be determined (iodimetry). Sulphurous acid solutions, however, change in strength so rapidly on account of spontaneous and continuous oxidation, that they cannot be made to serve as standards, and they have been entirely replaced by sodium thiosulphate solution, as recommended by Schwarz. This salt is easily obtained in a pure state, and may be weighed directly for a standard solution. The reaction in neutral or faintly acid solutions is as follows:—

---

[1] The weighed portion of an iron-ore should be ignited, gently at first, in a platinum crucible previous to being dissolved in hydrochloric acid, in order to destroy all organic matter present. Use 25 c.c. of acid and boil on the hot plate till the residue is fairly white.

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

sodium iodide and tetrathionate being formed.

The action of iodine on sodium thiosulphate in alkaline solution is irregular and excessive, even when the alkalinity is due to a bicarbonate.

As indicator starch solution is used, which gives with the slightest trace of free iodine, at ordinary temperatures, the well-known blue iodide of starch. Hydriodic or mineral acids and iodides have no influence upon the colour. Caustic alkalis destroy it.

Owing to the volatility of iodine, all iodimetric determinations should be carried out in glass stoppered bottles, which are kept closed except during titrations.

Wide-mouthed bottles of thin glass, of 250-300 c.c. capacity, answer well in most cases.

Iodimetric Processes are those in which iodine is a product of reaction, and by determining its amount the equivalent quantity of another element or group of elements is deduced. Free chlorine or bromine, for example, is determined by the equivalent amount of iodine that each sets free from potassium iodide solution. Similarly we may determine chlorites and hypochlorites (decomposed by hydrochloric acid and potassium iodide with separation of iodine); chromates, chlorates and the higher oxides of lead, manganese, nickel and cobalt (by treating each of these substances in a diminutive distillation flask with hydrochloric acid, collecting the evolved chlorine in potassium iodide solution and determining the iodine set free).

The principle of this method, namely, the use of iodine as an indirect oxidizing body by its action upon the elements of water, forming hydriodic acid with the hydrogen and liberating the oxygen in an active state, can be applied to the determination of substances which take up oxygen, and decolorize the iodine solution, such as sulphurous acid, sulphites, sulphuretted hydrogen, alkali thiosulphates and arsenites, stannous chloride, etc. These are brought into dilute solution, starch added, and the iodine delivered in with constant shaking or stirring until a point occurs at which a final drop of iodine colours the whole blue—a sign that the substance can take up no more iodine, and that the drop in excess has shown its characteristic effect upon the starch.

In iodine titrations the blue colour often reappears after the titration with thiosulphate has been completed. The most frequent cause of this is the presence of nitrogen peroxide derived from the air or water. Free or combined bromine, which acts more slowly than iodine upon thiosulphate, may have the same effect. Very slight traces of iodine do not act at once upon starch, but only after some time. In the absence of excess of thiosulphate the solution must, therefore, become blue again after some time.[1]

1. Preparation of the Decinormal Solution of Iodine.

12·692 gm. Iodine per litre.

Dissolve about 18 gm. of pure potassium iodide in about 30-50 c.c. of water in a stoppered litre flask and shake into it, through a dry funnel, 12·7 gm., or a little more, of pure re-sublimed iodine. Insert the stopper into the flask and shake in the cold till the iodine is completely dissolved. Then make up to the mark with water.

The iodine solution is best preserved in small stoppered bottles which should be completely filled, and kept in a cool and dark place. It should be used with a tap burette, as it makes rubber tubing hard and useless.

Iodine solution is generally standardized by a solution of sodium thiosulphate or of arsenious oxide, the strength of which has been accurately determined by pure iodine.

Barium thiosulphate (BaS_2O_3, H_2O) is also very useful for this purpose.[2] 267·506 gm. of the crystallized salt being equivalent to 126·92 gm. of iodine, 0·5 gm. of the former is equivalent to 0·2372 gm. of the latter. Weigh out 0·5 gm of the thiosulphate into a beaker, add water and run in the iodine solution cautiously, with continuous stirring, till only a few small crystals remain undissolved. Then add starch liquor and continue the addition of iodine solution till a permanent blue colour is obtained. If of exactly correct strength 18·7 (theoretically 18·69) c.c. of the iodine solution should be required

$$2BaS_2O_3 + I_2 = BaI_2 + BaS_4O_6$$

$$\text{Iodine} \times \left(\frac{64\cdot06}{253\cdot84} = \right) 0\cdot25236 = SO_2$$

$$\log.\ 0\cdot25236 = \bar{1}\cdot40203.$$

Pure barium thiosulphate is easily prepared by mixing together a warm solution of 50 gm. of sodium thiosulphate in 300 c.c. of water, and 40 gm. of barium chloride in a like volume of warm water; after stirring well, the salt soon separates in fine powdery crystals. These are collected in a funnel plugged with glass- or cotton-wool, repeatedly washed with cold water till all chlorine is removed, then dried at below 30° C. on a glass or porcelain plate until all extraneous moisture is removed; or the crystals may be treated, after thorough washing with alcohol and ether, as described below for sodium thiosulphate.

2. Decinormal Sodium Thiosulphate.

24·820 gm. per litre.

$$Na_2S_2O_3,\ 5H_2O = 248\cdot20.$$

It is not difficult either to manufacture or procure pure sodium thiosulphate, but there may be uncertainty as to extraneous water held within the crystals. In order to avoid this Meineke[1] recommends that the otherwise pure crystals be broken to coarse powder, washed first with pure alcohol, then with ether, and lastly dried in a current of dry air at ordinary temperature. The salt so prepared may be weighed directly, dissolved in a litre of distilled water, and then titrated with the iodine solution and starch. It is advisable to preserve the solution in the dark. After a time all solutions of thiosulphate undergo a slight amount of oxidation, and sulphur deposits upon the bottle; it is therefore always advisable to determine its strength previous to use. This may be done (i) against iodine in a solution previously standardized against standard alkali arsenite, (ii) against a weighed amount of specially prepared iodine, 0·5 gm of which requires 39·40 c.c. of a strictly $^N/_{10}$ solution of the thiosulphate, (iii) against iodine set free from an iodide by potassium dichromate solution of a certain strength.

---

[1] See *J. S. C. I.*, 1915, **34**, 1032

[2] Plimpton and Chorley. See *J.*, 1895, **20**, 111.

The strength of the thiosulphate solution is always recorded as 1 c.c. = x gm. iodine.

The solution preserves its strength better if an addition of 2 gm. of potassium bicarbonate to the litre is made and the solution kept in the dark

3. Starch Indicator.

One part of clean potato starch, or arrowroot, is first mixed with cold water into a smooth emulsion, then gradually poured into about 150 or 200 times its weight of boiling water, the boiling continued for a few minutes, then allowed to stand and settle thoroughly. The clear solution only is to be used as the indicator, of which a few drops only are necessary. The solution may be preserved for some time by adding to it a few drops of chloroform, and shaking well in a stoppered bottle, but it is preferable to use a fresh solution in all cases

A starch indicator which keeps indefinitely may be prepared by making use of the well-known fact that starch is soluble in a dilute solution of salicylic acid. Dissolve 1 gm. of salicylic acid in 100 c.c. of water, boil, pour into it 1 gm. of potato starch mixed with a little water, boil gently till the starch has dissolved, let cool somewhat, then dilute with cold water to a litre.

Lintner's soluble starch acts well as an indicator, as it gives at once a clear solution in boiling water. The colour which is produced with this form of starch is not quite so pure a blue as that given by a freshly made solution of ordinary starch, owing to the presence of some dextrin unavoidably produced in the preparation, but it is no hindrance to the end-point in practice. In iodimetric analyses it is always advisable in titrating the free iodine with thiosulphate or arsenious solution to delay adding the starch until the iodine colour is nearly removed; a much more delicate ending may be obtained and with very little starch

Influence of Iodides in Iodimetry.—It has been found that the delicacy of the indications in iodimetry turns upon the concentration of the iodide and that the amount of iodine necessary to give the blue colour with starch in presence of a suitable amount of potassium iodide increases with the dilution. Experience shows that while the presence of 0·3 gm. of potassium iodide in volumes not exceeding 300 c.c. is sufficient to give the maximum sharpness of readings the use of larger amounts of the iodide, within reasonable limits, is not harmful. Accurate results can be obtained at ordinary temperatures.

---

[1] *Chem. Z.*, **18**, 33.

Methylene Blue Indicator.—Sinnatt[1] points out that methylene blue forms a convenient indicator in iodimetric titrations in lieu of starch. In dilute solutions, when a solution of methylene blue is added to a solution of iodine in potassium iodide, the formation of an iodo-compound of the colouring matter is accompanied by a colour change from blue to yellowish-green, and finally to a clear yellowish-brown colour. On the completion of the iodine titration the blue colour recurs. With most reducing agents methylene blue is not reduced, but titanous chloride decolourizes it. 1 c c. of a 0·005 per cent solution of the indicator to 50 c.c. of liquid gives a convenient depth of colour for titrations.

USE OF STANDARD POTASSIUM IODATE IN IODIMETRY.

Iodine, free or evolved in reaction, may sometimes be conveniently determined by conversion to iodine chloride formed in the reaction of this iodine with sufficiently concentrated hydrochloric acid and a suitable oxidizer, potassium iodate in standard solution being the one best adapted to the purpose. The strength of an iodate solution may be fixed by determining the amount of iodine which is set free when a given amount of the iodate is acted upon in slightly acidified solution by an excess of potassium iodide, thus,

$$KIO_3 + 5KI + 6HCl = 6KCl + 3H_2O + 3I_2$$
$$\text{whence } KIO_3 = 6I.$$

Andrews[2] has shown, however, that the iodine set free in the reaction between a standard solution of iodate and an iodide may be converted to iodine monochloride by further action of the iodate in presence of sufficiently concentrated hydrochloric acid, and the amount of iodine acted upon may be found from the amount of iodate required to complete this reaction, thus

$$KIO_3 + 2KI + 6HCl = 3KCl + ICl + 3H_2O.$$

The end point of the reaction is shown by the disappearance of the iodine colour from chloroform or carbon tetrachloride (5 c.c.) shaken up with the solution. This process has the advantage that the reagent which sets free the iodine determines it also, and that the presence of chlorides or bromides does not interfere with the accuracy of the determination.

Ex. Determination of the strength of an approximately $^{N}/_{10}$ solution of potassium iodide.

Run from a burette 20 c.c. of the iodide solution into a 250 c.c. glass bottle provided with a glass stopper. Add 5 c.c. of chloroform and 30 c.c. of conc. hydrochloric acid. Into the mixture measure from a burette successive portions of the standard iodate solution, inserting the stopper and shaking the contents of the bottle vigorously between the additions of the iodate, until the violet colour of iodine in the chloroform just disappears. Results are calculated from the relation $KIO_3 = 2KI$, as given in the equation above.

---

[1] *Analyst*, 1910, **35**, 309

[2] *J. A. C. S.*, 1903, **25**, 756; *Anal*, 1903, **28**, 306.

The standard solution of potassium iodate used is made by dissolving 10·7 gm. (very nearly $\frac{1}{20}$ mol.) in water and diluting to 1 litre. It is standardized as indicated above.

Determination of Bromine.—Bromine reacts with an excess of potassium iodide according to the following equation :—

$$Br_2 + 2KI = 2KBr + I_2$$

$$\text{Hence } 79{\cdot}92 \text{ Br} = 126{\cdot}92 \text{ I, and I} \times 0{\cdot}6297 = \text{Br.}$$

When bromine in aqueous solution (best faintly acidulated with hydrochloric acid) is added to potassium iodide solution the iodine set free measures the bromine. To avoid loss by volatilization in the process the bromine solution should be delivered from a pipette, the tip of which is held close to the surface of the iodide solution contained in a flask or bottle provided with a glass stopper. On inserting the stopper and shaking the bottle the reaction is completed immediately and the free iodine is titrated either with standard thiosulphate or with standard arsenite—in the latter case after the addition of an excess of alkali carbonate.

I found × 0·6297 = Br.

Determination of Bromates. Bromic and hydriodic acids, formed in the interaction of potassium bromate, potassium iodide, and sulphuric acid, react together according to the equation

$$6HI + HBrO_3 = HBr + 3I_2 + 3H_2O.$$

Time of action, proportion of iodide to bromate, excess of acid and the concentrations are all, within limits, determining factors, but if free acid and a considerable excess of potassium iodide are present the reaction proceeds to completion within a reasonable time. Accurate results may be obtained as follows. To a solution measuring about 100 c.c. and containing an amount of potassium bromate not exceeding 0·14 gm. and about 3 gm. of iodide (i.e. nearly four times the amount theoretically required), 25 c.c. of sulphuric acid (1 : 1) or an equivalent amount of hydrochloric acid is added and the mixture, in a stoppered glass vessel, allowed to stand for half an hour. At the end of this time the reaction will have been completed and the liberated iodine is at once determined.

$$6I = KBrO_3\text{, and I} \times 0{\cdot}21932 = KBrO_3.$$

Determination of Iodates.—When potassium iodide in excess and dilute hydrochloric or sulphuric acid are added to the solution of an iodate, iodine is immediately set free according to the equation

$$MIO_3 + 5KI + 6HCl = 5KCl + MCl + 3H_2O + 3I_2.$$

The iodine set free may be titrated at once with standard thiosulphate, or it may be absorbed by an excess of standard arsenite, this excess being determined by titration with standard iodine.

$$6I = MIO_3\text{, and I} \times 0{\cdot}28104 = KIO_3.$$

Determination of Chromates and Dichromates.—Chromic acid is immediately reduced by potassium iodide in presence of hydrochloric acid to the green chromic chloride with separation of an amount of iodine equivalent to the oxygen lost by the chromic acid. The reactions are as follows:—

$$2K_2CrO_4 + 6KI + 16HCl = 10KCl + 2CrCl_3 + 8H_2O + 3I_2$$
$$K_2Cr_2O_7 + 6KI + 14HCl = 8KCl + 2CrCl_3 + 7H_2O + 3I_2$$
$$\text{or } K_2CrO_4 = 3I, \text{ and } I \times 0{\cdot}5100 = K_2CrO_4$$
$$K_2Cr_2O_7 = 6I, \text{ and } I \times 0{\cdot}3863 = K_2Cr_2O_7.$$

After diluting the solution sufficiently to prevent the green colour from masking the disappearance of the starch blue in the end reaction, standard thiosulphate is run in until the yellow is mostly removed, when starch is added and the addition of thiosulphate continued until the colour of the solution changes from blue to green.

Determination of Lead Dioxide.—In presence of 5 per cent. acetic acid, sodium acetate, and potassium iodide, lead dioxide, finely ground (if dry) or in hydrated form, is decomposed according to the equation

$$PbO_2 + 4HI = PbI_2 + 2H_2O + I_2.$$

If a large excess of the acetate is present with not too much potassium iodide the lead iodide will not precipitate, and upon further dilution the dissolved iodine may be titrated with standard thiosulphate.

Suitable proportions are about 0·5 gm. of lead dioxide, 1·2 gm. of potassium iodide, 10 gm. of sodium acetate, and 5 c.c. of acetic acid (5 per cent.). If lead iodide is precipitated it should be dissolved by more sodium acetate with a little water. After dilution to about 25 c.c. the clear solution of iodine is titrated with thiosulphate.

ANALYSIS OF SUBSTANCES BY DISTILLATION WITH HYDROCHLORIC ACID INTO ALKALI IODIDE.

THERE is a great variety of substances containing oxygen, which when boiled with hydrochloric acid yield chlorine, equivalent to the whole or a part only of the oxygen they contain according to circumstances. The chlorine so evolved, however, is not itself determined, but is conveyed by means of a suitable apparatus into a solution of potassium iodide, thereby liberating an equivalent quantity of iodine. This latter body is then determined by thiosulphate; the quantity so found is, therefore, a measure of the oxygen existing in the original substance, and consequently a measure of the substance itself. Analyses of this class may be made the most exact in the whole range of volumetric analysis, far out-stripping any gravimetric process.

The apparatus used for distilling the substances, and conveying the liberated chlorine into the alkali iodide, may possess a variety of forms, the most serviceable, however, being the kinds devised respectively by Bunsen, Fresenius, Mohr, and others, among which one of the best is so constructed as to avoid the use of corks or india-rubber, which are soon destroyed by the corrosive action of iodine and acid (see fig. 40).

Bunsen's arrangement consists of an inverted retort, into the neck of which the tube from the small distilling flask is passed.

Owing to the great solubility of HCl in the form of gas, the apparatus must be so constructed that when all chlorine is liberated and HCl begins to distil the liquid may not rush back into the flask owing to condensation.

The best preventive of this regurgitation is, however, one suggested by Fresenius, and applicable to each kind of apparatus; namely, the addition of a few pieces of pure magnesite. This substance dissolves but slowly in the hydrochloric acid, and so keeps up a constant evolution of CO_2, the pressure of which is sufficient to prevent the return of the liquid.

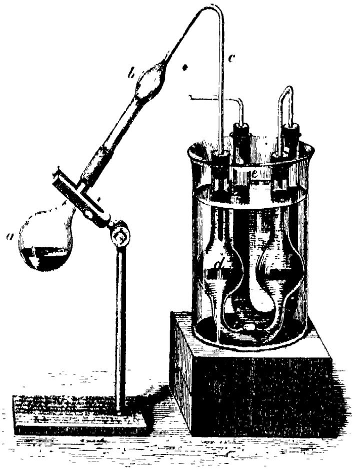

FIG. 35.

The apparatus contrived by Fresenius is shown in fig. 35, and is exceedingly useful as an absorption apparatus for general purposes.

Mohr's apparatus is shown in fig. 36, and is, on account of its simplicity of construction, very easy to use.

The distilling flask is of about 2 oz. capacity, and is fitted with a cork soaked to saturation in melted paraffin; through the cork the delivery tube containing one bulb passes, and is again passed through a common cork, fitted loosely in a stout tube about 12 or 13 inches long and 1 inch wide, closed at one end like a test tube. This tube, containing the alkali iodide, is placed in an hydrometer glass, about 12 inches high, and surrounded by cold water; the delivery tube, is drawn out to a fine point, and reaches nearly to the bottom of the condenser. No support or clamp is necessary, as the hydrometer glass keeps everything in position. The substance to be distilled is put into the flask, and covered with strong hydrochloric acid, the magnesite added, the condenser supplied with a sufficient quantity of iodide solution, and the apparatus put together tightly. Either an argand or common spirit lamp, or gas, may be used for heating the flask, but the flame must be manageable, so that the boiling can be regulated at will. In the case of the common spirit lamp it may be held in the hand, and applied or withdrawn according to the necessities of the case; the argand spirit or gas lamp can, of course, be regulated by the usual arrangements for the purpose. If the iodine liberated by the chlorine evolved should be more than will remain

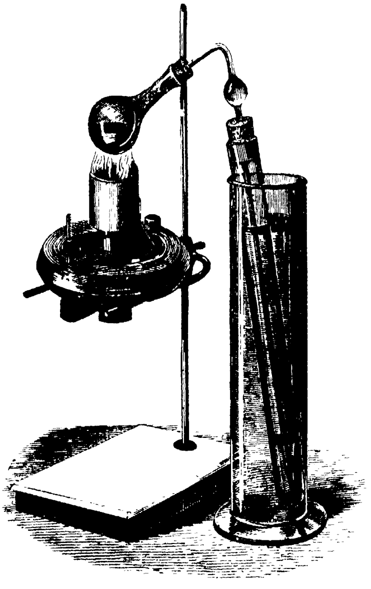

Fig. 36.

in solution, the cork of the condensing tube must be lifted, and more solution added. When the operation is judged to be at an end, the apparatus is disconnected, and the delivery tube washed out into the iodide solution, which is then emptied into a beaker or flask and preserved for titration, a little fresh iodide solution is put into the condenser, the apparatus again put together, and a second distillation commenced, and continued for a minute or so, to collect every trace of free chlorine present. This second operation is only necessary as a safeguard in case the first should not have been complete.

The solutions are then mixed together and titrated in the manner previously described. In all cases the solution must be cooled before adding the thiosulphate.

Instead of the large test tube, some operators use a **U** tube to contain the potassium iodide, having a bulb in each limb, but the latter is not necessary if magnesite is used.

The solution of potassium iodide may conveniently be made of such a strength that $\frac{2}{10}$ eq. or 32·2 gm. are contained in the litre. 1 c.c. will then be sufficient to absorb the quantity of free iodine representing 1 per cent. of oxygen in the substance analysed, supposing it to be weighed in the metric system. In examining peroxide of manganese, for instance, 0·4316 gm. would be used, and supposing the percentage of peroxide to be about sixty, 60 c.c. of iodide solution would be sufficient to absorb the chlorine and keep in solution the iodine liberated by the process; it is advisable, however, to have an excess of iodide, and, therefore, in this case, about 70 c.c. should be used. A solution of indefinite strength will answer as well, so long as enough is used to absorb all the iodine. It may sometimes happen that not enough iodide is present to keep all the liberated iodine in solution, in which case it will separate out in the solid form; more iodide, however, may be added to dissolve the iodine, and the titration can then be made as usual.

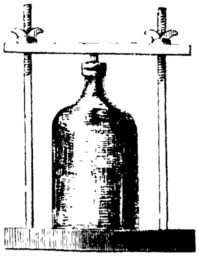

FIG. 37.

The process of distillation above described may be avoided in many cases. There is a great number of substances which, by mere digestion with hydrochloric acid and potassium iodide at an elevated temperature, undergo decomposition quite as completely as by distillation. For this purpose a strong bottle with a very accurately ground stopper is necessary; and as the ordinary stoppered bottles of commerce are not sufficiently tight, it is better to regrind the stopper with a little *very fine* emery and water. It must then be tested by tying the stopper tightly down and immersing in hot water; if any bubbles of air find their way through the stopper the bottle is useless. The capacity may vary from 30 to 150 c.c., according to the necessities of the case.

The stopper may be secured by fine copper binding-wire, or a kind of clamp contrived by Mohr may be used, as shown in fig. 37; by means of the thumb-screws the pressure upon the stopper may be increased to almost any extent.

The substance to be examined, if in powder, is put into the bottle with pure flint pebbles or small garnets, so as to divide it better, and a sufficient quantity of *saturated* solution of potassium iodide and pure hydrochloric acid added; the stopper is then inserted, fastened down, and the bottle suspended in a water bath, and the water is gradually heated to boiling by a gas flame or hot plate as may be most convenient. When the decomposition is complete the bottle is removed, allowed to cool somewhat, then placed in cold water, and after being shaken, emptied into a beaker, and the liquid diluted by the washings for titration.

The salts of chloric, iodic, bromic, and chromic acids, together with many other compounds, may be as effectually decomposed by digestion as by distillation, many of them even at ordinary temperatures. Recently precipitated oxides, or the natural oxides when reduced to fine powder, are readily dissolved and decomposed by very weak acid in the presence of potassium iodide (Pickering).

The potassium iodide used in the various analyses must be absolutely free from iodate and free iodine, or, if otherwise, the effect of the impurity must be ascertained by a blank experiment.

ARSENIOUS ACID AND IODINE.

$As_2O_3 = 197{\cdot}92$.[1]

THE principle upon which this method of analysis is based is the fact that when arsenious acid is brought into contact with iodine in the presence of water and free alkali, it is converted into arsenic acid, the reaction being—

$$As_2O_3 + 2I_2 + 2K_2O = As_2O_5 + 4KI.$$

The alkali must be in sufficient quantity to combine with the hydriodic acid set free, and it is necessary that it should exist in the state of bicarbonate, as caustic or monocarbonated alkalis interfere with the colour of the blue iodide of starch used as indicator.

If, therefore, a solution of arsenious acid containing starch is titrated with a solution of iodine in the presence of an alkali bicarbonate, the blue colour does not appear until all the arsenious acid is oxidized into arsenic acid. In like manner, a standard solution of arsenious acid may be used for the determination of iodine or other bodies which possess the power of oxidizing it.

The chief value, however, of this method is found in the determination of free chlorine existing in the so-called "chloride of lime," chlorine water, hypochlorites of lime, soda, etc., in solution; generally included under the term Chlorimetry.

Preparation of the $^N/_{10}$ Solution of Alkali Arsenite.

4·948 gm As_2O_3 per litre

1 c.c. = 0·003546 gm. Cl
1 c.c. = 0·012692 gm. I.

The iodine solution used is the same as that described on p. 136.

The corresponding solution of alkali arsenite is conveniently prepared by dissolving 4·948 gm. of the purest sublimed arsenious oxide, reduced to powder, in a concentrated solution of 4 gm. of caustic potash or soda and making up to a litre by the addition of 100 c.c. of a saturated solution of potassium or sodium bicarbonate and the required volume of water. The arsenic goes much more readily into solution with this small amount of hydroxide (which does not affect the titration with iodine) than with bicarbonate alone. If the mixture need warming, it should not be heated above 60° C.

---

[1] Properly As_4O_6 mol. wt. 395·84.

In order to test this solution, 20 c.c. are put into a beaker with a little starch indicator, and the iodine solution run in from a burette until the blue colour appears. If exactly 20 c.c. are required, the solution is strictly decinormal; if otherwise, the necessary factor must be found for converting it to that strength. The value of the solution is best expressed in terms of its iodine equivalent, which, if of exact strength, is

1 c.c. = 0·012692 gm. iodine.

A carefully prepared standard arsenite solution retains its strength practically indefinitely.

Iodized Starch-paper.—This is used as an external indicator in the determination of free chlorine. It is made as follows:—

1 gm. of starch is boiled with 100 c.c. of water, the solution filtered and 0·1 gm. of KI added to the filtrate. Filter paper is then soaked in this solution and dried on a porcelain or similar plate at 40°-50°. For the spotting test the paper should be moistened, as the reaction is much cleaner and more delicate with moist than with dry paper. Three or four pieces of the paper are spread on a glass plate and any excess of water allowed to flow off; they are then ready for spotting.

PART IV.

ANALYSIS BY PRECIPITATION.

THE general principle of this method of determining the quantity of any given substance is alluded to on p. 3, and in all instances the procedure is such that the body to be determined forms an insoluble precipitate with a titrated reagent. The end of the reaction is, however, determined in one of three ways :—

1. By adding the reagent until no further precipitate is produced, as in the determination of chlorine by silver.

2. By adding the reagent in the presence of an indicator contained either in the liquid itself, or brought externally into contact with it, so that the slightest excess of the reagent shall produce a characteristic reaction with the indicator; as in the determination of silver with sodium chloride by the aid of potassium chromate, or with thiocyanate and ferric sulphate, or that of phosphoric acid with uranium by the aid of potassium ferrocyanide as indicator.

3. By adding the reagent to a clear solution until a precipitate is formed, as in the determination of cyanogen by silver.

The first of these methods can only be applied with great accuracy to silver and chlorine determinations. Very few precipitates have the peculiar quality of chloride of silver, namely, almost perfect insolubility, and the tendency to curdle readily by shaking, so as to leave the menstruum clear. Some of the most insoluble precipitates, such as barium sulphate and calcium oxalate, are unfortunately excluded from this class, because their finely divided nature prevents their ready and perfect subsidence.

In all these cases, therefore, it is necessary to find an indicator, which brings them into class 2.

The third class comprises only two processes; viz., the determination of cyanogen by silver, and that of chlorine by mercuric nitrate.

Since the determination of chlorine by precipitation with silver, and that of silver by thiocyanic acid can be used in many cases for the indirect determination of many other substances with great exactness, the preparation of the necessary standard solutions will now be described.

DETERMINATION OF CHLORINE.

1. Decinormal Solution of Silver Nitrate.

16·989 gm. $AgNO_3$ per litre.

10·788 gm. of pure silver are dissolved in pure dilute nitric acid with gentle heat in a flask, into the neck of which a small funnel is dropped to prevent loss of liquid by spurting. When solution is complete, the funnel must be washed inside and out with distilled water into the flask, and the liquid diluted to a litre; but if it be desired to use chromate as indicator in any analysis, the solution must be neutral. In the latter case the solution of silver in nitric acid is evaporated to dryness, and the residue dissolved in a litre; or, preferably, 16·989 gm. of pure crystallized silver nitrate, previously heated to 120° C. for ten minutes, are dissolved in a litre of distilled water. Fused nitrate of silver is, however, best of all for this purpose. 17·1 gm. of the fused salt are dissolved in a litre of distilled water, so as to make a solution rather stronger than is required. A burette is then filled with the solution and it is titrated with 25 c.c. of decinormal sodium chloride solution in a white porcelain dish, using potassium chromate as indicator. It is then diluted with water to exact strength, and finally tested as before.

2. Decinormal Solution of Sodium Chloride.

5·846 gm. NaCl per litre.

5·846 gm. of pure sodium chloride are dissolved in distilled water, and the solution made up to a litre.

1 c.c. = 0·005846 gm. NaCl,
or 0·003546 gm. Cl.

There are two methods by which the end of the reaction may be determined :—

(*a*) By adding silver solution cautiously, and well shaking after each addition till no further precipitate is produced. For details see under Silver (4).

(*b*) By using a few drops of solution of pure potassium chromate as indicator, as devised by Mohr. If the pure salt is not at hand, some drops of silver nitrate solution should be added to the solution of the ordinary salt, to remove chlorine, and the clear liquid used.

The method *b* is exceedingly serviceable, on the score of saving both time and trouble. The solutions must be neutral, and cold. When, therefore, acid is present in any solution to be examined, it should be neutralized with pure sodium or calcium carbonate, or the latter may be added in very slight excess.[1] Liquids containing much organic matter in solution or suspension may be made slightly alkaline by the addition of lime-water (free from chlorides), evaporated to dryness in a platinum dish, and the residue gently ignited. The latter is then treated with hot water, filtered and washed, when a colourless solution is obtained which, after cooling, is suitable for titration.

Method of Procedure: To the neutral or faintly alkaline solution two or three drops of a cold saturated solution of chromate are added,

---

[1] Silver chromate is sensibly soluble in the presence of alkali or alkaline earthy nitrates, especially at a high temperature; sodium and calcium nitrates have the least effect; ammonium, potassium, and magnesium nitrates the greatest. See also Forbes Carpenter (*J. S. C. I.*, 1886, **5**., 286).

EXAMPLE: 0·25 gm. pure sodium carbonate was dissolved in water, and hydrochloric acid added till in excess; it was then dried on the water bath till no further vapours of acid were evolved, the resulting white mass was heated for a few minutes to about 150° C., dissolved and made up to 300 c.c. 100 c.c. required 15·7 c.c. $^N/_{10}$ silver, this multiplied by 3 gave 47·1 c.c. which multiplied by the $^N/_{10}$ factor for sodium carbonate (= 0·0053) gave 0·2496 gm. instead of 0·25 gm.

Indirect Determination of Potassium and Sodium existing as Mixed Chlorides.—It is a problem of frequent occurrence to determine the relative quantities of potassium and sodium existing in mixtures of the two chlorides, such as occur, for instance, in urine, manures, soils, waters, etc. The actual separation of potash from soda by means of platinum is tedious, and not always satisfactory.

The following method of calculation is frequently convenient, since a careful determination of the chlorine present in the mixture is the only labour required; and this can most readily be accomplished by $^N/_{10}$ silver solution and chromate, as previously described.

(1) The weight of the mixed pure chlorides is accurately found and noted.

(2) The chlorides are then dissolved in water, and very carefully titrated with $^N/_{10}$ silver and chromate for the amount of chlorine present, which is also recorded, the calculation is then as follows:—

The weight of chlorine is multiplied by the factor 2·1026; from the product so obtained is deducted the weight of the mixed chlorides found in (1). The remainder multiplied by 3·6305 will give the weight of sodium chloride present in the mixture

(log 2·1026 = 0·32276; log 3·6305 = 0·55997).

The weight of sodium chloride deducted from the total as found in (1) will give the weight of potassium chloride.

Sodium chloride × 0·5303 = Soda (Na_2O).
Potassium chloride × 0·6317 = Potash (K_2O).

The principle of the calculation, which is based on the atomic constitution of the individual chlorides, is explained in most of the standard works on general analysis. Indirect methods like this can only give useful results when the atomic weights of the two substances differ considerably, and when the proportions present are approximately equal.

Another method of calculation in the case of mixed potassium and sodium chlorides is as follows:—

The weight of the mixture is first ascertained and noted; the chlorine is then found by titration with $^N/_{10}$ silver, and calculated to NaCl; the weight so obtained is deducted from the original weight of the mixture, and the remainder multiplied by 2·42857 will give the potassium.

DETERMINATION OF SILVER IN ACID SOLUTION (Volhard's Method).

THIS excellent and most accurate method has been devised by Volhard[1] and fully described by the author, and has been favourably noticed by many other well-known chemists. It differs from Mohr's chromate method in that the silver solutions may contain free nitric acid, which renders it of great service in indirect analyses.

---

[1] *Liebig's Ann. d. Chem.*, **190**, 1.

This method is based on the fact that when solutions of silver and an alkali thiocyanate are mixed in the presence of a ferric salt, so long as silver is in excess the thiocyanate of that metal is precipitated, and any brown ferric thiocyanate which may form is at once decomposed. When, however, the thiocyanate is added in the slightest excess, brown ferric thiocyanate is formed, and asserts its colour even in the presence of much free acid. The method may, of course, be used for the determination of silver, and, by the residual process, for the determination of substances which are completely precipitated by silver. In cases where chlorine is precipitated by excess of silver, and the excess has to be found by thiocyanate, experience has proved that it is absolutely necessary to filter off the chloride and titrate the filtrate and washings. If this be not done the solvent effect of the thiocyanate upon the AgCl will give inaccurate results. This fact seems to have been overlooked at the time the method was first introduced.

It may be used for the determination of silver in the presence of copper up to 70 per cent.; also in presence of antimony, arsenic, iron, zinc, manganese, lead, cadmium, bismuth, and also cobalt and nickel, unless the proportion of these latter metals is such as to interfere by intensity of colour.

It may further be used for the indirect determination of chlorine, bromine, and iodine, in presence of each other, existing either in minerals or inorganic compounds, and for copper, manganese, and zinc; these will be noticed under their respective heads.

For the determination of chlorine in water by Volhard's method see Water Analysis section.

1. Decinormal Ammonium or Potassium Thiocyanate.

This solution cannot be prepared by weighing the thiocyanate direct, owing to the deliquescent nature of the salts; therefore about 9 gm. of the ammonium, or 10 gm. of the potassium, salt may be dissolved in a litre of water as a basis for getting an exact solution, which must be finally adjusted by a standard decinormal silver solution.

The standard solution so prepared remains of the same strength for a very long period if preserved from evaporation.

2. Decinormal Silver Solution.

This is the same as described in a preceding section (p. 146), and may contain free nitric acid if made direct from metallic silver, but nitrous acid must be removed by boiling, as the latter forms a red compound with thiocyanic acid liable to be mistaken for ferric thiocyanate.

3. Ferric Indicator.

This may consist simply of a saturated solution of iron alum to which nitric acid has been added; or may be made by oxidizing ferrous sulphate with nitric acid, evaporating with excess of sulphuric acid to dissipate nitrous fumes, and dissolving the residue in water so that the strength is about 10 per cent.

5 c.c. of either of these solutions are used for each titration, which must always take place at ordinary temperatures.

4. Pure Nitric Acid.

This must be free from the lower oxides of nitrogen, secured by diluting the usual pure acid with about one-fourth of its volume of water, and boiling till perfectly colourless. It should then be preserved in the dark.

The quantity of nitric acid used in the titration may vary within wide limits, and seems to have no effect upon the precision of the method.

METHOD OF PROCEDURE: 50 c.c. of $^{N}/_{10}$ silver solution are measured into a flask, diluted somewhat with water, and 5 c.c. of ferric indicator added, together with about 10 c.c. of nitric acid. If the iron solution should cause a yellow colour, the nitric acid will remove it. The thiocyanate is then delivered in from a burette; at first a white precipitate is produced rendering the fluid of a milky appearance, and as each drop of thiocyanate falls in, it produces a reddish-brown cloud which quickly disappears on shaking. As the point of saturation approaches, the precipitate becomes flocculent and settles easily; finally, a drop or two of thiocyanate produces a faint brown colour which no longer disappears on shaking. If the solutions are correctly balanced, exactly 50 c.c. of thiocyanate should be required to produce this effect.

The colour is best seen by so holding the flask as to catch the reflected light of a white wall or a suspended sheet of white paper.

PART V.

APPLICATION OF THE FOREGOING PRINCIPLES OF ANALYSIS TO SPECIAL SUBSTANCES.

ALUMINIUM.

$Al = 27 \cdot 1.$

ALUMINIUM salts (e.g. the alums and aluminium sulphates used in dyeing and paper making) may be titrated for alumina in the absence of iron (except for mere traces) by mixing the acid solutions with a tolerable quantity of sodium acetate, then a known volume in excess of $^{N}/_{10}$ phosphate solution (20·9 gm. of ammonio-sodium phosphate per litre), and heating to boiling, without filtration; the excess of phosphate is found at once by titration with standard uranium. If iron in any quantity is present, it may be determined in a separate portion of the substance, and its amount deducted before calculating the alumina. The latter is precipitated as $AlPO_4$, and any iron in like manner as $FePO_4$. Each c.c. of $^{N}/_{10}$ phosphate = 0·00513 gm. Al_2O_3. This method is only available for rough purposes.

Baeyer's Method.—As originally proposed, this process for determining alumina in alums and aluminic sulphates was carried out by two titrations, a measured portion of the solution being first treated with an excess of normal soda sufficient to dissolve the precipitate of hydrate of alumina first formed. It was then diluted to a definite volume, one half being titrated with normal acid and litmus, the other half with tropæolin OO, the difference being calculated to alumina.

A considerable improvement, however, has been made by using phenolphthalein as the indicator, one titration only being necessary. The method is based on the fact that if to a solution of alumina, containing the indicator, normal soda is added in excess, or until the red colour is produced, and normal acid be then added until the colour disappears, the volume of acid so required is less than the soda originally added in proportion to the quantity of alumina present.

The volume of acid which so disappears is in reality the quantity necessary to combine with the alumina set free by the alkali; and if this deficient measure of acid be multiplied by the factor 0·01703 ($\frac{1}{6}$ mol. wt. of Al_2O_3), the weight of alumina will be obtained. This factor is given on the assumption that the normal sulphate Al_23SO_4 is formed.

The titration must take place in the cold and in dilute solutions.

Very fair technical results have been obtained by me with potash and ammonia alums and the commercial sulphates of alumina.

Alumina existing as aluminate of alkali in caustic soda, for instance, may be very well determined by taking advantage of the fact that such alumina is quite indifferent to methyl orange, but reacts acid with phenol-phthalein. This fact has been recorded by Thomson and others, but the priority of discovery appears to be due to Baeyer,[1] who, however, used litmus in the place of phenolphthalein, and tropæolin OO instead of methyl orange.

Cross and Bevan,[2] in their examination of caustic soda for alumina, found by experiment that the mean of the difference between the titration with methyl orange and that with phenolphthalein required the factor 0·0205 per c.c. of normal acid for the alumina, pointing to the salt as $2Al_2O_3 : 5SO_3$.

The determination of the alumina in caustic soda has given rise to much discussion between even very experienced operators, notably Cross and Bevan and Lunge,[3] but the former chemists have proved, as far as possible by various methods, the accuracy of their views that the formula given above is correct. The method adopted by them consists in boiling the weighed sample with a slight excess of standard acid, allowing to cool and titrating back with standard soda and phenolphthalein. The acid so consumed represents the total alkali present. To a similar portion a slight excess of acid is added and titrated back with soda and methyl orange.

Schmatolla[4] recommends as the most reliable method for the determination of acids combined with aluminium the titration of the boiling solution of the aluminium salt with alkali carbonate till phenolphthalein turns distinctly red, titrating back with acid if necessary.

Determination of Free Acid.—Alum cakes or aluminic sulphates of various kinds often contain free H_2SO_4, and many methods have been proposed for its determination. Baeyer titrates a 10 per cent. solution of the substance in water with normal soda and tropæolin OO or methyl orange.

R. Williams[5] adopts the alcohol method, digesting the substance for at least twelve hours with strong alcohol, filtering off and washing with the same, and titrating the solution without dilution or evaporation with $N/_{10}$ acid and phenolphthalein.

Beilstein and Grosset[6] have examined with great care all the methods proposed for this purpose, and have devised one which gives very good technical results.

METHOD OF PROCEDURE: 1 to 2 gm. of substance is dissolved in 5 c.c. of water, 5 c.c. of a cold saturated neutral solution of ammonium sulphate added, and stirred for a quarter of an hour. 50 c.c. of 95 per cent. alcohol are then added, the mixture thrown on a small filter, and washed with 50 c.c. of the same alcohol. The filtrate is evaporated on the water bath, the residue dissolved in water and titrated with $^{N}/_{10}$ alkali and litmus. The whole of the neutral aluminic sulphate is precipitated as ammonia alum, the alcohol contains all the free acid.

---

[1] *Z. a. C.*, **24**, 512.

[2] *J. S. C. I.*, 1889, **8**, 252.

[3] *Z. angew. Ch.*, 1890, **227**, 293.

[4] *Ber.*, 1905, **38**, 985; and *J. S. C. I.*, 1905, **24**, 349.

[5] *C. N.*, **56**, 194.

[6] *Z. a. Ch.*, **29**, 73; and *J. S. C. I.*, 1890, **9**, 416.

As indicator, Congo red may be used instead of litmus, employing it in very dilute solution and as an outside indicator.

T. J. I. Craig's[1] method for the determination of free acid and basic alumina in aluminium salts is based on the fact that an excess of neutral potassium fluoride decomposes aluminium salts, forming two stable compounds neutral to phenolphthalein, whilst any free acid remains unaltered, thus--

$$Al_2(SO_4)_3 + (xH_2SO_4) + 12KF = 2(AlF_3, 3KF) + 3K_2SO_4 + (xH_2SO_4).$$

The precipitated aluminium potassium fluoride is insoluble in the presence of a moderate excess of potassium fluoride, and is not appreciably attacked by dilute acid or dilute caustic alkali.

The free acid in salts of iron and zinc may be determined by this method, but larger excess of potassium fluoride is necessary.

For details of the method see loc. cit.

Iodimetric Method of A. Stock.[2]—Reagents required: A mixture of equal parts of a 25 per cent. solution of potassium iodide and a saturated solution of iodate (containing 6-7 per cent. of the salt). Standard sodium thiosulphate solution.

When a mixture of potassium iodide and iodate is added to a solution of an aluminium salt, a precipitate of aluminium hydrate is formed and a quantity of iodine set free according to the following equation:—

$$Al_2(SO_4)_3 + 5KI + KIO_3 + 3H_2O = 2Al(OH)_3 + 3K_2SO_4 + 3I_2.$$

The reaction, although commencing rapidly in the cold, is not complete for some days, especially in dilute solutions. The rapidity is increased if the liberated iodine be removed by means of standard thiosulphate, especially when warmed. By heating the solution on a water-bath the reaction is complete in a few minutes, even in the case of very dilute solutions. The process is not available in a solution containing tartaric, oxalic, or phosphoric acid, but boric acid does not appear to interfere.

METHOD OF PROCEDURE: The solution is first neutralized with sodium hydrate, as it must be neither too acid nor alkaline, then some of the iodide and iodate reagent added. After five minutes the sodium thiosulphate solution is run in from a burette until the solution becomes decolorized, then a further quantity of the iodide reagent added to make sure of complete precipitation. After heating on a water-bath for half an hour, the flocculent precipitate is filtered off and the titration of the filtrate with standard thiosulphate completed.

T. V. Kovscharova[3] uses $^{N}/_{10}$ sodium thiosulphate solution which he adds in excess after the iodide and iodate mixture. The liquid is then heated to boiling and the excess of thiosulphate titrated with $^{N}/_{10}$

---

[1] *J. S. C. I.*, 1911, **30**, 184.

[2] *Compt. rend.* **130** [4], 175, *J. S. C. I.*, 1900, **19**, 276; *J. C. S.*, 1900, **78**, ii., 247, 315.

[3] *J. C. S.*, 1915, **108**, ii., 582 (abstr.).

iodine solution. Trustworthy results are obtained when (1) the excess of thiosulphate solution is small; (2) the solution is as nearly neutral as possible; and (3) the heating on the water-bath is not continued for longer than 20-30 minutes.

From the above equation we see that 761·52 parts of iodine correspond to 102·2 parts of Al_2O_3. Hence 1 gm. of iodine = 0·1342 gm. of Al_2O_3.

ANTIMONY.

Sb = 120·2

I. Conversion of Antimonious Acid in Alkaline Solution into Antimonic Acid by Iodine (Mohr).

This method, due to **Mohr**, is quite satisfactory for tartar emetic, antimony oxide and some other antimony compounds, but it fails when applied to alloys in which antimony is not the principal constituent, but is present to the extent of 5 per cent. to 20 per cent. only. The presence of tin is a disturbing factor, but its influence may be counteracted by a large excess of an alkali tartrate.

Antimonious oxide, or any of its compounds, is brought into solution as tartrate by tartaric acid and water; the excess of acid neutralized by sodium carbonate; then a cold saturated solution of sodium bicarbonate added, in the proportion of 10 c.c. to about 0·1 gm. Sb_2O_3; to the clear solution starch is added and $^N/_{10}$ iodine until the blue colour appears. No delay must occur in the titration when the bicarbonate is added, otherwise a portion of the metal is precipitated as antimonious hydrate, upon which the iodine has little effect. **Dunstan** and **Boole**[1] have proved that the accurate determination of the antimony in tartar emetic may be secured by this method, using the precautions mentioned.

The colour disappears after a little time, therefore the first appearance of a reddish tint with starch is accepted as the true measure of iodine required. Greater accuracy is attained by adding an excess of 1 c.c. of $^N/_{100}$ iodine and titrating back with thiosulphate.

1 c.c. $^N/_{10}$ iodine = 0·006 gm. Sb.

Mohr's process for the determination of antimonious oxide is both convenient and exact. It depends on the reaction

$$Sb_2O_3 + 2I_2 + 2H_2O = Sb_2O_5 + 4HI.$$

which takes place in a solution containing an excess of alkali bicarbonate. The above equation shows that 120·2 parts of antimony (as Sb_2O_3) are equivalent to 253·84 parts iodine, and the weight of iodine found multiplied by 0·4735 = Sb.

For the determination of *antimonic acid* and its salts, **G. von Knorre**[2] gives the following method as accurate:—

Method of Procedure: The solution of the salt, strongly acidified with hydrochloric acid, is treated in a roomy flask with strong solution of sodium sulphite, added gradually in small portions. It is then vigorously boiled until all SO_2 is expelled, a drop of phenolphthalein is added, then caustic potash until red; this is in turn removed by a small excess of tartaric acid. Sodium bicarbonate is then added, and the titration with iodine carried out in the usual way.

---

[1] *Pharm. Jour.*, Nov., 1888.

[2] *Zeit. angew. Chem.*, 1888, 155.

Determination of Antimony in presence of Tin (Type and Britannia metal, etc.).[1]—The finely divided alloy is dissolved in strong hydrochloric acid by heat, adding frequently small quantities of potassium chlorate. The liquid is boiled to remove free chlorine, cooled, a slight excess of strong solution of potassium iodide added, and the liberated iodine determined by standard thiosulphate.

Clark[2] has made experiments as to the value of Mohr's process in antimony ores and alloys, and makes the following remarks with respect to them :—

> Mohr's process leaves nothing to be desired in point of sharpness and accuracy, and the chief object of my experiments has been to ascertain the best condition for the application of this method to the determination of antimony in ores and metals. I have proved by experiments that the presence of lead, even in large quantity, has no influence on the result, but the process is affected by iron, and by copper, arsenic, and tin in the lower state of oxidation. The following is a short summary of my results :—
>
> I. In the case of pure antimony ores practically free from arsenic and iron, the ore may be dissolved in HCl, heated till all the H_2S has been driven off, then mixed with tartaric acid or Rochelle salt, rendered alkaline by bicarbonate of soda, and titrated with $^{N}/_{10}$ iodine solution, as recommended by Mohr. 1 gm. antimony ore containing traces of Fe gave antimony 46·77 per cent. Another 1 gm. antimony ore containing traces of Fe gave antimony 46·80 per cent.
>
> II. When the ore contains more than traces of iron, it is dissolved in HCl, precipitated with H_2S, filtered, washed, re-dissolved in HCl, and the antimony titrated in an alkaline tartrate solution as before.
>
> III. When the ore contains arsenic, which is by no means a rare occurrence, it is dissolved in strong HCl containing sufficient ferric chloride to decompose the sulphides, and the arsenic is distilled off; the antimony is then precipitated with H_2S, filtered, washed, re-dissolved in HCl, and titrated with $^{N}/_{10}$ iodine in an alkaline tartrate solution. The arsenic in the distillate can also be titrated with iodine in presence of excess of bicarbonate of soda.
>
> IV. When an alloy or sulphide contains tin as well as arsenic and antimony, it may be dissolved in HCl and Fe_2Cl_6, the arsenic distilled off as before, and the antimony precipitated with metallic iron (which should be as pure as possible, steel filings answer well). The precipitated antimony, after being filtered and washed, is then dissolved in HCl with the assistance of a little chlorate of potash, filtered from any insoluble impurity derived from the iron, precipitated with H_2S, filtered, washed, dissolved in HCl, boiled to expel H_2S, and titrated with $^{N}/_{10}$ iodine in an alkaline tartrate solution.
>
> The antimony ore referred to above, when treated in this way, gave the following results :—
>
> 1 gm. gave antimony 46·62 per cent. Another 1 gm. gave antimony 46·68 per cent.

---

[1] See also H. Yockey, *J. A. C. S.*, 1906, 1435

[2] *J. S. C. I.*, 1896, **15**, 255.

Clark has also discovered a modified iodimetric process which may be used where the original process is inadmissible.

When antimony is dissolved in HCl with the assistance of chlorate of potash, nitric acid, or bromine, the oxidizing agent converts the antimony into the highest state of oxidation, on which account it is necessary to reduce it again to render it suitable for the application of Mohr's process. It has been discovered, however, that when antimony is dissolved in HCl with the assistance of iodine, no reducing agent is required, as iodine in an acid solution does not oxidize antimony beyond Sb_2O_3, so that after boiling off the excess of iodine Mohr's process can be at once applied to the solution.

This action of iodine is of very great importance, as it simplifies very much the determination of antimony in alloys containing lead and tin, as the tin is oxidized by the iodine to the stannic state, and the lead has no influence on the result. In applying the process, a weighed quantity of the alloy is treated with HCl so long as there is any action, then solid iodine is added in small quantities at a time, and heat applied till complete solution has taken place. The excess of iodine is removed by boiling, and the solution cooled, diluted, and mixed with a little starch. Should the addition of starch produce a blue colour in the acid solution owing to the presence of a trace of free iodine, a very weak solution of sulphide of sodium is added drop by drop till the blue colour disappears. It is then mixed with Rochelle salt, rendered alkaline with sodium carbonate and titrated with $^N/_{10}$ iodine in the presence of a considerable excess of sodium bicarbonate.

In this way good results were obtained with white metal and alloys containing large proportions of lead; but if copper is present the result is too low, and the copper should be removed by converting the metals into sulphides, and dissolving out the antimony by caustic soda or potash.

2. Oxidation by Potassium Permanganate (Low).

$$5SbCl_3 + 16HCl + 2KMnO_4 = 5SbCl_5 + 2KCl + 2MnCl_2 + 8H_2O.$$

It is probably correct to say that the method of Low,[1] or one or other of its modifications,[2] has superseded all other methods for the determination of antimony in the presence of tin, lead, copper, etc., in Babbitt metal, type metal, antimonial lead, etc.

METHOD OF PROCEDURE: Weigh out 1 gm. of the finely-divided alloy into a 300 c.c. conical flask; add 3 gm. of pure potassium sulphate and 12 c.c. of concentrated sulphuric acid. Heat until the alloy is completely decomposed; this may take thirty minutes or longer. Cool add ·25 gm. pure tartaric acid, and heat again until the solution becomes colourless and the lead sulphate (if present) quite white. Cool, add 50 c.c. of water and 12 c.c. concentrated hydrochloric acid, and warm until all antimony and tin are in solution. Add 60 c.c. of cold water, cool thoroughly, and titrate with standard permanganate solution until a pink flush indicates the end-point. This pink colour may disappear after a time, but no more permanganate should be added, the first definite pink being taken as the end point.

---

[1] *J. A. C. S.*, 1907, **29**, 66.

[2] Bulletin, No. 109, revised, U.S. Dept. of Agriculture, Bureau of Chemistry: Demorest, *J. Ind. and Eng. Chem.*, 1913, **5**, 842, McCabe, *ibid.*, 1917, **9**, 42.

The permanganate solution should be standardized against pure finely-powdered metallic antimony or anhydrous tartar emetic.

1 c.c. of a solution containing 5·27 gm. of potassium permanganate per litre = 1 per cent of antimony in 1 gm. of substance.

The presence of tin does not influence the results, which are accurate to within 0·1 per cent. Large amounts of lead and small amounts of copper do not interfere. If much iron is present, the alloy should be dissolved in nitric acid to remove any danger of ferrous sulphate being found in the final solution. The nitric acid is removed by boiling with 10 c.c. of sulphuric acid and 2-4 gm. of potassium sulphate, after which a little tartaric acid is added, and the boiling continued until the organic matter is completely destroyed. The antimony will then be in its lower state of oxidation.

Arsenic, if present, is measured as antimony. The arsenic may be separately determined and its equivalent amount of antimony deducted. Or the antimony and tin may be separated by treatment with an alkali sulphide, their sulphides being precipitated from this solution by the addition of sulphuric acid, and heated with sulphuric acid and potassium sulphate as above.

In the titration with permanganate Demorest and McCabe (loc. cit.) recommend that an excess of permanganate be run in, titrating back with, say, ferrous sulphate solution.

3. Distillation of Antimonious or Antimonic Sulphide with Hydrochloric Acid, and Titration of the evolved Sulphuretted Hydrogen (Schneider).

When either of the sulphides of antimony is heated with hydrochloric acid in Bunsen's, Fresenius's, or Mohr's distilling apparatus (figs. 35, 36), for every eq. of antimony present as sulphide, 3 eq. of H_2S are liberated. If, therefore, the latter be determined, the quantity of antimony is ascertained.

METHOD OF PROCEDURE: The antimony to be determined is brought into the form of ter- or penta-sulphide (if precipitated from a hydrochloric acid solution, tartaric acid must be previously added to prevent the precipitate being contaminated with chloride), which, together with the filter containing it, is put into the distilling flask with a tolerable quantity of hydrochloric acid not too concentrated. The absorption tube contains a mixture of caustic soda or potash with a definite quantity of $^{N}/_{10}$ arsenious acid solution in sufficient excess to retain all the sulphuretted hydrogen evolved. The flask is then heated to boiling, and the operation continued till all evolution of sulphuretted hydrogen has ceased; the mixture is then poured into a beaker, and acidified with hydrochloric acid, to precipitate all the arsenious sulphide. The whole is then diluted to, say, 300 c.c., and 100 c.c. taken with a pipette, neutralized with sodium carbonate, some bicarbonate added, and titrated for excess of arsenious acid with $^N/_{10}$ iodine and starch. The separation of antimony may generally be ensured by precipitation as sulphide. If arsenic is precipitated at the same time, it may be removed by treatment with ammonium carbonate.

4. Titration with Standard Potassium Bromate (Györy).[1]

This method was originally devised for the valuation of Fowler's solution and of tartar emetic; hence it is applicable to both arsenic and antimony.

$$2KBrO_3 + 2HCl + 3Sb_2O_3 = 2KCl + 2HBr + 3Sb_2O_5.$$

Reagent required:

Decinormal potassium bromate—2·784 gm. of the pure crystals dried at 110° C. are dissolved in water and made up to 1 litre.

$$1 \text{ c.c.} = 0{\cdot}004948 \text{ gm. } As_2O_3$$
$$1 \text{ c.c.} = 0{\cdot}00721 \text{ gm. } Sb_2O_3 = 0{\cdot}006 \text{ gm. } Sb.$$

The titration is performed in a solution acidified with HCl. For a 1 per cent. solution of arsenious acid an equal volume of dilute HCl (1 : 2) is used; but in the case of antimony more acid must be taken in order to prevent the precipitation of the antimony with increasing dilution during titration. Thus, for 0·3 gm. of tartar emetic 25 c.c. or more of the dilute acid should be added. Methyl orange is added to the solution as indicator. In each case the slightest excess of bromate completely decolorizes the red solution in consequence of the liberation of bromine. The bromate solution should be added gradually, especially towards the end. The presence of tin and of considerable quantities of iron and copper interferes with this method.

J. B. Duncan[2] recommends the following procedure.—

He standardizes the $^N/_{10}$ potassium bromate solution by dissolving 0·3 gm. of pure finely divided antimony in 20 c.c. HCl and a few drops of bromine in a covered 400 c.c. beaker, keeping the liquid warm and occasionally shaking till the metal is dissolved. Then boil off excess of bromine, cool a little, and add about 0·75 gm. of sodium sulphite. Boil the mixture down to about half its volume to drive off SO_2. (In the case of alloys this latter operation will also remove any arsenic present.) Rinse the cover and sides of the beaker with hot water, and add a little HCl. Then heat the liquid to boiling and run in the decinormal bromate from a burette until nearly all the antimony has been oxidized. Now add three drops of methyl orange and continue the addition of bromate until the colour of the methyl orange is destroyed. About 50 c.c. will be required, as 1 c.c. of $^N/_{10}$ bromate = about 0·006 gm. Sb. The exact value of 1 c.c. is thus obtained. The process is strongly recommended for the analysis of hard lead, alloys, ores of antimony, etc. 0·3 gm. is taken for the determination, and the solution is effected as described above.

---

[1] *Z. a. C.*, 1893, **32**, 415.

[2] *C. N.*, 1907, **95**, 49.

For the determination of antimony in antimonial lead Nissenson and Siedler[1] modify the method as follows. They dissolve the alloy in hydrochloric acid saturated with bromine, reduce the antimony with sodium sulphite, add more hydrochloric acid, and titrate the hot solution with the standard potassium bromate, using indigo solution as indicator.

5. Determination of Antimony Pentoxide and its Compounds (Weller).

This is the converse of method 1. The pentachloride is distilled with strong HCl and KI in one of the forms of distilling apparatus (see figs. 35 and 36), and the separated iodine titrated with $^{N}/_{10}$ thiosulphate.

Notes on the foregoing Methods. E. Schmidt[2] especially recommends methods 2 and 4 for technical purposes.

Beckett[3] finds that the volumetric determination of antimony with iodine gives very concordant results, but these are only correct when the older atomic weight of antimony (Sb = 122) is used. When the atomic weight Sb = 120·2 is taken the results are about 1 per cent. too low.

Determination of Antimony in its Sulphide Preparations.—Howard and Harrison[4] propose to convert the antimony sulphide into sodium metantimonate by fusion with sodium peroxide, the antimony salt being then reduced and determined iodimetrically, whilst the sulphur is determined as sulphate.

ARSENIC.

$As = 74·96$. $As_2O_3 = 197·92$. $As_2O_5 = 229·92$.

1. Oxidation by Iodine (Mohr).

The principle upon which the determination of arsenious oxide by iodine is based is explained on p. 144.

Experience has shown that in the determination of arsenious compounds by the method there described it is necessary to use sodium bicarbonate for rendering the solution alkaline, as in the case of antimony.[5]

Method of Procedure: To a neutral aqueous solution, add about 20 c.c. of saturated solution of sodium bicarbonate to every 0·1 gm. or so of As_2O_3, and then titrate with $^{N}/_{10}$ iodine and starch. When the solution is acid, it may be neutralized with sodium carbonate, then the necessary quantity of bicarbonate added, and the titration completed as before.

Procedure for Arsenic Acid: This is best done by dissolving the acid in water and boiling with potassium iodide in the presence of hydrochloric acid in large excess until all iodine vapours are dissipated.

---

[1] *Chem. Zeit.*, 1903, **27**, 749.

[2] *Ibid.*, 1910, **34**, 453.

[3] *C. N.*, 1910, **102**, 101.

[4] *Ph. J.*, 1909, **83**, 142.

[5] Washburn (*J. A. C. S.*, 1908, **30**, 31, and *Analyst*, 1908, **33**, 102) has studied Mohr's method. He suggests the use of sodium phosphate instead of bicarbonate.

The H_3AsO_4 is completely reduced to H_3AsO_3. The liquid is then cooled, sodium carbonate added to neutrality, then some bicarbonate, and the arsenious acid titrated with iodine in the usual way. Younger[1] has verified this method and proved that the reduction is complete; he also states that when the boiled solution cools, the liberation of a slight amount of iodine occurs, which may be prevented by using a few c.c. of glycerin. Of course the arsenic acid must contain no nitric acid, nitrates, or similar interfering bodies.

$$1 \text{ c.c. } ^{N}/_{10} \text{ iodine} = 0{\cdot}004948 \text{ gm. } As_2O_3,$$
$$\qquad = 0{\cdot}005748 \text{ gm. } As_2O_5.$$

The Determination of Arsenic in Alkali Arsenates.—It was originally proposed by Mohr to effect this by passing sulphur dioxide through the solution so as to reduce the arsenic to arsenious acid, boiling off the SO_2, and determining the arsenious acid by iodine as just described. This process, however, was not widely adopted, as it was found defective in many instances for the reason that the mere passing of the gas through the liquid did not ensure complete reduction of the acid.

Holthof[2] and McKay[3] have experimented largely on this method of determining arsenic, and Holthof proved that various forms of arsenic, on being converted into arsenic acid, would bear evaporation to dryness with HCl without loss, and that arsenic sulphide could be oxidized by strong nitric acid, or with HCl and $KClO_3$, to arsenic acid, and reduced to the lower state of oxidation by copious treatment with SO_2, the method being to add 300 or 400 c.c. of strong solution of SO_2, digest on the water-bath for two hours, then boil down to one-half, and when cool add sodium bicarbonate, and titrate with iodine.

McKay shortens the method considerably by placing the mixture in a well-stoppered bottle, tying down the stopper, and digesting in boiling water for one hour. At the end of that time the bottle is removed and allowed to cool somewhat, then emptied into a boiling flask, diluted with about double its volume of water, and boiled down by help of a platinum spiral to one-half. The liquid is cooled, diluted, and either the whole or an aliquot portion titrated with iodine in the usual way.

For quantities of material representing about 0·1 gm. As, 30 c.c. of saturated solution of SO_2 will suffice, and the reduction may therefore be made in a bottle holding 50 or 60 c.c. (fig. 37). The results are satisfactory. In the case of titrating commercial alkali arsenates, which often contain small quantities of arsenious acid, this must be determined first, and the amount deducted from the total obtained after reduction.

A. Williamson[4] has devised the following ready method as being applicable to commercial arsenates, and has made use of the reaction which takes place between arsenic and hydriodic acids in strong acid solution. In these circumstances arsenic acid is quantitatively reduced with liberation of iodine. The reaction is

$$As_2O_5 + 4HI = As_2O_3 + 2H_2O + 2I_2.$$

---

[1] *J. S. C. I.*, 1890, **9**, 158. [2] *Z. a. C.*, 1883, **22**, 378. [3] *C. N.*, 1886, **53**, 221-243.

[4] *Journal of the Society of Dyers and Colourists*, May, 1896.

It was found that the reduction is complete only in strongly acid solution, and that if such a solution be diluted the reverse reaction takes place to a certain extent, a portion of the arsenious becoming oxidized to arsenic acid. The iodine may, however, be determined before dilution by means of thiosulphate, and in the absence of other bodies capable of liberating iodine it may be taken as a measure of the arsenic acid. The acid solution may then be neutralized, and the arsenite titrated with iodine after addition of sodium bicarbonate. This serves as a check on the thiosulphate titration.

The reduction may be effected either in hydrochloric or sulphuric acid solution, but in either case a considerable excess of acid must be present, otherwise the reduction is incomplete.

As commercial sodium arsenate usually contains some nitrate, experiments were made to ascertain whether the presence of this salt interferes with the accuracy of the thiosulphate titration. A pure solution of arsenate was prepared as before, and 1 gm. of sodium nitrate added. 25 c.c. of this solution were then treated with potassium iodide and hydrochloric acid, and the iodine titrated with thiosulphate as before. The arsenic acid calculated from the thiosulphate consumed was 100·3, instead of 100. It is evident that the presence of nitrate causes little or no liberation of iodine in the cold, but if the arsenate is digested with hydrochloric acid and potassium iodide in a closed bottle immersed in boiling water the iodine liberated is considerably in excess of that corresponding to the arsenic acid. In this case, the quantity of thiosulphate consumed is of no value. The arsenic can, however, be accurately determined by titrating the arsenite after the iodine has been decolorized.

Instead of hydrochloric acid, 15 c.c. of a mixture of sulphuric acid and water, in equal volumes, may be used. Since the addition of sulphuric acid causes the solution to become slightly heated, it is cooled before titrating the iodine. The results are practically the same as with hydrochloric acid.

Not less than 3 gm. potassium iodide should be added, or complete reduction is not immediately effected. The presence of small quantities of nitrate does not interfere with the accuracy of the thiosulphate titration. Complete reduction can be brought about with 2 gm. potassium iodide and 10 c.c. of sulphuric acid, if the solution is heated for five minutes on the steam bath. A portion of the iodine volatilizes, but no arsenic is lost. The iodine is exactly decolorized with thiosulphate, the solution neutralized and titrated with iodine in the ordinary manner.

Procedure with Commercial Arsenate of Soda: 10 gm. are dissolved to 1 litre, and the arsenic acid in 25 c.c. determined by one of the methods given above. The thiosulphate titration records only the arsenic previously existing as arsenic acid. The small proportion of As_2O_3 which usually exists is ascertained by direct titration. When this is calculated to arsenic acid, and added to that found by thiosulphate, the results approximate very closely to those found by titrating the arsenic.

Determination of Arsenic in presence of Tin.—If both these elements are present in the lower state of oxidation, the tin may be oxidized with iodine in strong acid solution, the arsenic being unaffected. Rochelle salt is then added, the solution neutralized, and the arsenite titrated with iodine.

Example: 25 c.c. of $^{N}/_{10}$ sodium arsenite were mixed with 25 c.c of hydrochloric acid, and 3 gm. stannous chloride added. The tin was then exactly oxidized with standard iodine, and the arsenic titrated in the alkaline solution. 24·9 c.c. of $^{N}/_{10}$ iodine were required.

If they are present in the highest state of oxidation, the arsenic may be reduced by one of the methods given under the determination of arsenic acid. The stannic salt is not affected.

It is thus possible to determine the arsenic in a mixture of arsenate and stannate of soda. In presence of a considerable quantity of tin, however, the complete reduction of the arsenic acid is not effected quite as readily as when tin is absent. The following method has given good results:—

4 or 5 gm. of the mixture are dissolved in as small a quantity of HCl as possible, an equal weight of tartaric acid is dissolved in the solution, which is then diluted to 250 c.c. (If the tartaric acid is not added a precipitate forms on dilution which contains both tin and arsenic.) 25 c.c. of this solution are then mixed with 3 gm. potassium iodide and 25 c.c. HCl, sp. gr. 1·16, and the solution heated on the steam bath for two or three minutes to ensure the complete reduction of the arsenic acid. The liberated iodine is exactly decolorized with thiosulphate, and the arsenic determined by titration with iodine in the neutralized solution. A mixture of arsenate and stannate in equal quantities and containing a known percentage of arsenic gave 28·57 instead of 28·75 per cent. of arsenic acid.

2. Oxidation by Potassium Dichromate (Kessler).

The arsenious compound is mixed with $^{N}/_{10}$ dichromate in excess in presence of hydrochloric acid and water, in such proportion that at least $\frac{1}{6}$ of the total volume consists of hydrochloric acid (sp. gr. 1·12).

The excess of dichromate is found by a standard solution of pure ferrous sulphate or ferrous ammonium sulphate, with potassium ferricyanide as indicator; the quantity of dichromate reduced is, of course, the measure of the quantity of arsenious converted into arsenic acid.

$$1 \text{ c.c. } ^{N}/_{10} \text{ dichromate} = 0·004948 \text{ gm. } As_2O_3.$$

In cases where the direct titration of the hydrochloric acid solution cannot be accomplished, the arsenious acid is precipitated with H_2S (with arsenates at 70° C.), the precipitate well washed, the filter and the precipitate placed in a stoppered flask, together with a saturated solution of mercuric chloride in hydrochloric acid of 1·12 sp. gr., and digested at a gentle heat until the precipitate is white, then water added in such proportion that not less than $\frac{1}{6}$ of the volume of liquid consists of concentrated HCl; $^{N}/_{10}$ dichromate is then added, and the titration with standard ferrous solution completed as usual.

3. Indirect Determination by Distilling with Chromic and Hydrochloric Acids (Bunsen).

The principle of this very exact method depends upon the fact that when potassium dichromate is boiled with concentrated hydrochloric acid, chlorine is liberated in the proportion of 3 eq. to 1 eq. of chromic acid.

If, however, arsenious acid is present, but not in excess, the chlorine evolved is not in the proportion mentioned above, but so much less as is necessary to convert the arsenious into arsenic acid.

$$As_2O_3 + 4Cl + 2H_2O = As_2O_5 + 4HCl.$$

Therefore every 4 eq. of chlorine short of the quantity yielded when dichromate and hydrochloric acid are distilled alone represent 1 eq. arsenious acid. The operation is conducted in some form of the apparatus described on p. 140 *et seq.*

4. By Precipitation as Uranium Arsenate (Bödeker).

Method of Procedure: The arsenic must exist in the state of arsenic acid (As_2O_5), and the process is in all respects the same as for the determination of phosphoric acid, devised by Neubauer, Pincus, and myself (*infra*). The strength of the uranium solution may be ascertained and fixed by pure sodium or potassium arsenate, or by means of a weighed quantity of pure arsenious acid converted into arsenic acid by evaporation with strong nitric acid, then neutralized with alkali, and dissolved in acetic acid. The method of titration is precisely the same as with phosphoric acid; the solution of uranium should be titrated upon a weighed amount of arsenical compound, bearing in mind here, as in the case of P_2O_5, that the titration must take place under precisely similar conditions as to quantity of liquid, the amount of sodium acetate and acetic acid added, and the depth of colour obtained by contact of the fluid under titration with the ferrocyanide solution.

Boam[1], who has had large experience in the examination of arsenical ores, recommends this method as being rapid and accurate, and carries it out as follows:—

Method of Procedure: 1 to 1·5 gm. of dried and powdered ore is boiled to dryness with 20-25 c.c. of strong nitric acid; when cool about 30 c.c. of 30 per cent. caustic soda solution is added and boiled for a few minutes; then diluted, filtered, and made up to 250 c.c. 25 c.c. of the liquid are acidified with a solution containing 10 per cent. of sodium acetate in 50 per cent. acetic acid, and heated nearly to boiling, then titrated with the standard uranium as usual. For this latter, the same authority recommends what he terms a fourth-normal solution of uranium, containing 17·1 gm. uranium acetate, and 15 c c. glacial acetic acid made up to 2 litres with water, 1 c.c. being equal to 1·25 mgm. As. But if the method has to be considered accurate, this suggestion can scarcely be adopted, since the uranium acetate of commerce is of indefinite hydration; and moreover, to ensure exactitude, it is necessary that the titration should be carried out with the same proportions of saline matters, acetic acid, etc., as existed when originally standardizing the uranium. I, therefore, unhesitatingly recommend that the uranium should be standardized with a known weight of pure arsenic or arsenate in the presence of the same proportions of sodium hydrate and acetate, acetic acid, etc., as will actually be used in the analysis of an ore. The method may be used for all ores which can be attacked by nitric acid. It is also available for iron pyrites containing tolerable quantities of arsenic; the ferric arsenate being readily decomposed by excess of NaHO, thus allowing the ferric hydrate to be filtered off free from As.

---

[1] *C. N.*, 1890, **61**, 219.

The solution of arsenic acid must, of course, be free from metals liable to give a colour with the indicator and from phosphates. Alkalis, alkaline earths, and zinc are of no consequence, but it is advisable to add nearly the required volume of uranium to the liquid before heating. The arsenic acid must be separated from all bases which would yield compounds insoluble in weak acetic acid.

The AsH_3 evolved from Marsh's apparatus may be passed into fuming HNO_3, evaporated to dryness, the arsenic acid dissolved in water (antimony, if present, is insoluble), then titrated cautiously with uranium in presence of free acetic acid and sodium acetate as above described.

5. By Standard Silver as Arsenate.

This method has been devised by Pearce of the Colorado Smelting Company, and is as follows:—

Method of Procedure: The finely-powdered substance for analysis is mixed in a large porcelain crucible with from six to ten times its weight of a mixture of equal parts of sodium carbonate and potassium nitrate. The mass is then heated with a gradually increasing temperature to fusion for a few minutes, allowed to cool, and the soluble portion extracted by warming with water in the crucible, and filtering from the insoluble residue. The arsenic is in the filtrate as alkali arsenate. The solution is acidified with nitric acid and boiled to expel CO_2 and nitrous fumes. It is then cooled to the ordinary temperature, and almost exactly neutralized as follows:—Place a small piece of litmus paper in the liquid: it should show an acid reaction. Now gradually add strong ammonia till the litmus turns blue, avoiding a great excess.[1] Again make slightly acid with a drop or two of strong nitric acid; and then, by means of very dilute ammonia and nitric acid, added drop by drop, bring the solution to such a condition that the litmus paper, after having previously been reddened, will, in the course of half a minute, begin to show signs of alkalinity. The litmus paper may now be removed and washed, and the solution, if tolerably clear, is ready for the addition of silver nitrate. If the neutralization has caused much of a precipitate (alumina, etc.), it is best to filter it off at once, to render the subsequent filtration and washing of the arsenate of silver easier.

A solution of silver nitrate (neutral) is now added in slight excess; and after stirring a moment to partially coagulate the precipitated arsenate, which is of a brick-red colour, the liquid is filtered, and the precipitate washed with cold water. The filtrate is then tested with silver and dilute ammonia, to see that the precipitation is complete.

The object is now to determine the amount of silver in the precipitate, and from this to calculate the arsenic. The arsenate of silver is dissolved on the filter with dilute nitric acid (which leaves undissolved any chloride of silver), and the filtrate titrated, after the addition of ferric sulphate, with thiocyanate (p. 150).

---

[1] Canby neutralizes with an emulsion of zinc oxide. *J. C. S.*, 1890, **58**, 923.

From the formula $3\ Ag_2O.As_2O_5$, 647·2 parts Ag = 149·92 parts As, or Ag : As = 1 : 0·2316.

A modification of the above method is suggested by J. F. Bennett[1] in order to avoid some sources of inaccuracy. He found that it was very difficult to obtain neutrality by either of the processes given, and, by avoiding ammonia, phenolphthalein could be used as an indicator.

Waddell[2] and his collaborators as the result of their investigation of the process express the opinion that Canby's modification gives too low results, whilst that of Bennett is likely to yield too high figures, but that both of the methods may be so amended that they will give practically concordant results. Waddell recommends fusion of the substance with ten or twelve times its weight of sodium peroxide, extraction of the fusion with water, and making up the volume of the solution to a litre or half a litre. A sufficient aliquot quantity is then taken to require at least 14 c.c. of the thiocyanate solution. If Canby's method is being used, the alkaline solution is neutralized with nitric acid, a very slight excess added, and, after addition of silver nitrate, this small excess is neutralized by zinc oxide.

If the Bennett modification is being followed, the alkaline solution of the arsenate is acidified with nitric acid, made slightly alkaline with pure caustic soda, and then very slightly acid with acetic acid before precipitating the arsenic as silver arsenate.

Owing to the large amount of arsenate of silver formed from a small quantity of arsenic (nearly six times by weight), it is not at all necessary or even desirable to work with large amounts of substance. 0·5 gm. is usually sufficient for the determination of the smallest quantity of arsenic; and where the percentage is high as little as 0·1 gm. may be taken with advantage. The method has been used with very satisfactory results on the sulphide of arsenic obtained in the ordinary course of analysis.

Substances such as molybdic and phosphoric acids, which behave similarly to arsenic under this treatment, interfere, of course, with the method. Antimony, by forming sodium antimonate, remains practically insoluble and without effect.

6. Determination of Arsenious Sulphide by Iodine.

J. and H. S. Pattison[3] have shown that the separation of arsenic as sulphide from many metals, viz., lead, tin, cadmium, antimony, and bismuth, is complete when made in concentrated hydrochloric acid (sp. gr. 1·16-1·17). The subsequent determination is carried out by the the authors as follows :—

---

[1] *J. A. C. S.*, 1899, **21**, 431.

[2] *J. Eng. and Ind. Chem.*, 1919, **11**, 939-941.

[3] *J. S. C. I.*, 1898, **17**, 211.

METHOD OF PROCEDURE : The precipitate is collected on asbestos in a Gooch crucible and washed with cold water until free from hydrochloric acid. The asbestos felt with the adhering precipitate is then placed in the small beaker; the crucible is wiped out with a little clean ignited asbestos, which is also put into the beaker. 10 or 15 c.c. of concentrated sulphuric acid (sp. gr. about 1·83), free from arsenic are then poured into the beaker, which is then placed without a cover on a hot plate or on a wire gauze over a small Bunsen flame in a good draught closet. As soon as the acid reaches the temperature at which it begins to fume, the arsenious sulphide becomes rapidly decomposed; at first both sulphuretted hydrogen and sulphurous acid are given off (if a cover be put on the beaker the mutual decomposition of these two gases causes a deposition of sulphur on the sides of the beaker). The evolution of sulphuretted hydrogen is over in a few seconds, but the sulphur dioxide takes longer to expel, depending upon the quantity of arsenious sulphide and of free sulphur that may have been mixed with the precipitate. As soon as the decomposition of the arsenious sulphide begins, the liquid becomes darkened in colour, and the heating, which may be brought to and kept at the verge of ebullition of the acid, is continued until this dark colour disappears, when it will be found that all the sulphurous acid has been expelled. It is of the utmost importance that all sulphurous acid should be eliminated at this stage. This takes about 10 to 20 minutes with precipitates of sulphide weighing about 0·02 gm. and nearly free from free sulphur. Arsenious acid remains in solution in the sulphuric acid and the amount is determined by cooling the acid, diluting with water, nearly neutralizing the acid with concentrated sodium hydrate solution, and then completing the neutralization and rendering alkaline with an excess of sodium bicarbonate, and finally titrating with standard iodine solution and starch. The iodine solution must be standardized against an approximately equal quantity of arsenious acid, to which the same amount of sulphuric acid has been added as was used for the decomposition of the arsenious sulphide precipitate. As sulphuric acid alone usually requires a few tenths of a cubic centimetre of centinormal iodine solution to be added to it before the blue colour of iodide of starch forms, a blank experiment with the stock of acid in use should be made once for all. It was found the best plan to avoid breaking up the asbestos felt, and if possible to put it in the beaker so that the side on which the precipitate lies is on the bottom of the beaker. This prevents the precipitate from becoming detached from the felt and floating to the top of the acid or creeping up the side of the beaker.

This method was used for six months in the course of daily work, alongside of determinations made by weighing the sulphide precipitate, or, after having separated the arsenic by Fischer's distillation process, by titrating the distillate (previously rendered alkaline) with iodine solution, and the results were very concordant.

Experiments show that there is no loss of arsenious acid by volatilization when arsenious sulphide is decomposed by heating with strong sulphuric acid in the manner described.

Determination of Arsenic in Iron Ores, Steel, and Pig Iron (J. E. Stead).—The best method of separating arsenic from iron solutions is undoubtedly that of distilling with hydrochloric acid and ferrous chloride.

Stead found, after many trials and experiments, that if the distillation is conducted in a special manner the whole of the arsenic may be obtained in the distillate, unaccompanied with any traces of ferrous chloride, and that if the hydrochloric acid is nearly neutralized with ammonia, and finally completely neutralized with sodium bicarbonate, the arsenic can be determined with iodine in the usual manner.

The standard solutions required are :—

Arsenious oxide, 0·66 gm. (= 0·5 gm. elemental arsenic) of pure arsenious oxide in fine powder is weighed and placed in a flask, with 2 gm. of sodium carbonate and 100 c.c. of boiling distilled water, and the liquid boiled till all the arsenious oxide has dissolved. When cool, 2 gm. of sodium bicarbonate are added and diluted to 1 litre.

1 c.c. = 0·0005 gm. As.

Iodine solution. 1·7 gm. of pure iodine is dissolved in 2 gm. of potassium iodide and water, the solution diluted to one litre, then standardized by titrating 20 c.c. of the arsenious solution. If pure iodine has been used, 20 c.c. of the solution should be required just to produce a permanent blue with starch.

These solutions keep fairly well without alteration for several months. It is advisable, however, to ascertain periodically the value of the iodine solution by titrating it with the arsenic solution.

METHOD OF PROCEDURE FOR STEEL: From 1 to 50 gm. of the steel in drillings are introduced into a 30-ounce flask, and a sufficient quantity of equal parts of strong hydrochloric acid and water is added to dissolve it. The mouth of the flask is closed with a rubber stopper carrying a safety tube and a tube to convey the gas evolved into the Winkler's spiral absorption tubes, containing a strong saturated solution of bromine in water.

The tube is filled to one-third of its length with the solution, and about ½ c.c of free bromine is run in to replace the bromine which is consumed or carried out with the passing gas.

The contents of the flask are now gently heated to such a degree that a steady but not rapid current of gas passes through the bromine solution.

In about one hour the whole of the steel will be dissolved, and when no more evolution of hydrogen can be observed, the liquid in the flask is well boiled, so as completely to drive all the gas into and through the bromine solution.

The absorption tube is now disconnected, and the bromine solution containing that part of the arsenic which has passed off as gas is rinsed out into a small (100 c.c.) beaker, the excess of bromine is gently boiled off, and the clear colourless solution poured into the flask. About 0·5 gm. of zinc sulphide is now dropped into the iron solution and the contents are violently shaken for about three minutes, by which time the whole of the arsenic will be in the insoluble state, partly as sulphide, and partly as a black precipitate of possibly free arsenic and arsenide of iron.

It has been found that violent agitation for a few minutes is quite as efficacious in effecting the complete separation of arsenic sulphide as the method of passing a current of CO_2 through the solution to remove the excess of hydric sulphide, or allowing it to stand ten or twenty hours to settle out.

The insoluble precipitate is now rapidly filtered through a smooth filter-paper, and the flask is rinsed with cold distilled water. The precipitate usually does.

not adhere to the filter, and in such cases the paper is spread out flat upon a porcelain slab, and the arsenic compounds are rinsed off with a fine jet of hot water into a small beaker. The precipitate is now dissolved in bromine water and a drop or two of HCl.

The bromine solution now containing all the arsenic is gently boiled to expel the bromine, and it is then poured into a 10-ounce retort and distilled with ferrous chloride and hydrochloric acid.

The apparatus used consists of an ordinary Liebig's condenser, but the retort has its neck bent to an angle of about 150°, and this is attached to the condenser, so that any iron mechanically carried over may run back. By this device, the distillate will never contain more than the very slightest trace of iron.

The solution containing the arsenic having been run into the retort, the beaker is washed out and the washings are also poured in. If the solution is much above 20 c.c. in bulk, it is advisable to add a strong solution of ferrous chloride containing about 0·5 gm. of iron in the ferrous state, and for this purpose nothing answers so well as a portion of the steel solution remaining after separating the arsenic, which is first well boiled to free it from hydric sulphide, and should contain about 10 per cent. of soluble iron as ferrous chloride. 5 c.c. of this solution will contain the necessary amount of iron to add to the retort. After adding the chloride, it is best to boil down the solution to about 20 c.c. before adding any HCl, taking care, of course, to collect the liquid that distils over. When the necessary concentration has been effected, 20 c.c. of strong HCl are run in, and the distillation is continued till all excepting about 10 c.c. has passed over. A further quantity of 20 c.c. mixed with 5 c.c. of water is run in, and this is all distilled over. At this point, as a rule, all the arsenic will have passed into the distillate, but it is advisable to make quite certain, and to add a third portion of acid and water, and to distil it over. If the distillation has not been forced, the distillate will be quite colourless. The arsenic in the distillate will exist as arsenious chloride, accompanied with a large excess of hydrochloric acid. A drop of litmus is put into this solution, and strong ammonia is run in until alkaline. It is now made slightly acid with a few drops of HCl, and a slight excess of solid bicarbonate of soda is dropped in. The contents of the flask are now cooled by a stream of water, and, after adding a clear solution of starch, the standard iodine solution is run in from a burette till a deep permanent blue coloration is produced.

If the steel or iron contains much arsenic, a smaller quantity, say, 1 or 2 gm., may be dissolved in nitric acid of 1·20 specific gravity and the solution evaporated to dryness, the residue being dissolved in hydrochloric acid, and the solution transferred to the retort, and distilled directly with ferrous chloride and hydrochloric acid, care being taken that the distillation is not forced, so as to avoid any of the iron solution passing over into the distillate.

METHOD OF PROCEDURE FOR PIG-IRON: In testing pig-irons, they may be dissolved in nitric acid and evaporated to dryness, or be treated in a flask with HCl exactly in the manner described above; but it is advisable, if the latter method is adopted, after treating the voluminous mass of silica and graphite, etc., with bromine and hydrochloric acid, to filter off the insoluble matter and distil the clear solution.

METHOD OF PROCEDURE FOR IRON ORES: In testing ores, it is only necessary to place the powdered ore directly into the retort, and distil at once with HCl and ferrous chloride, taking care to place a few small pieces of broken pipe-stems also in the vessel, to avoid bumping.

If the ore contains much manganese, it is advisable to dissolve it in a separate vessel to liberate and expel the chlorine, and then to transfer it into the retort.

The time taken to test iron or steel need not exceed two hours, and for iron or other ores not much more than half an hour.

It is quite possible accurately to determine as small a quantity as 0·002 per cent. of arsenic by this method.

When dissolving steels in dilute HCl, if there is no rust on the sample or ferric chloride present in the acid, and the presence of air is carefully avoided, as a rule only about one-tenth of the total arsenic present passes off with the gas.

A very simple and accurate method of determining a small amount of arsenic when it exists in the form of freshly precipitated sulphide is suggested by F. Platten.[1] It consists in simply boiling the sulphide with pure water for a period of from 1 to 3 hours, or until the liquid is quite colourless, and all the H_2S dissipated. The arsenic will then exist wholly as As_2O_3, and may be titrated direct with $^{N}/_{100}$ iodine, and a slight amount of sodium bicarbonate as usual.

Both this and Stead's method have been proved to give identical results, when carried out by separate skilled operators on the same samples of material.[2]

7. Titration by Potassium Bromate (Györy).

See under Antimony, p. 160.

8. Titration by Potassium Iodate (Andrews).

See p. 138 (Applicable to Antimony).[3]

$$2AsCl_3 + KIO_3 + 5H_2O = 2H_3AsO_4 + KCl + ICl + 4HCl$$

Add to the arsenious solution an amount of strong hydrochloric acid sufficient to make the acidity of the entire mixture at the end of the titration not less than 11 per cent. of HCl, and not more than 20 per cent. HCl. Too little acidity fails to prevent the hydrolysis of the iodine monochloride, whilst with an excess the reaction takes place too slowly. Run in standard potassium iodate solution (after the addition of 5 c.c. of chloroform) rapidly at first, with constant shaking, then slowly until the iodine coloration of the chloroform disappears and does not reappear after standing for five minutes.

$$\begin{aligned}1 \text{ c.c. decinormal iodate solution} &= 0{\cdot}0099 \text{ gm. } As_2O_3\\ &= 0{\cdot}0075 \text{ gm. As.}\end{aligned}$$

Since copper does not interfere, it is possible to titrate the arsenic direct in Paris Green, for example, and other arsenite preparations. Jamieson[4] takes 0·15 to 0·4 gm. of the sample, mixed with 30 c.c. of hydrochloric acid (sp. gr. 1·19), 20 c.c. of water and 6 c.c. of chloroform, and titrates as above, using $^{N}/_{30}$ potassium iodate (3·567 gm. KIO_3 per litre).

---

[1] *J. S. C. I.*, 1894, **13**, 321.

[2] See also A. H. Low, "Determination of Antimony and Arsenic in Ores," *J. A. C. S.*, 1906, **28**, 1715; and Norton and Koch, "Determination of Arsenic and Antimony in the presence of Organic Matter," *ibid.*, 1905, **27**, 1247.

[3] *Vide* Jamieson, *J. Ind. and Eng. Chem.*, 1911, **3**, 250.

[4] *Ibid.*, 1918, **10**, 290.

9. Determination of Arsenic in Organic Compounds.

Little, Cahen, and Morgan,[1] find the most satisfactory process to be a combination of Pringsheim's[2] method of oxidation by sodium peroxide and Gooch and Browning's volumetric method.[3]

METHOD OF PROCEDURE: 0·2-0·3 gm. of the finely powdered substance is mixed in a nickel crucible with 10-15 gm. of sodium carbonate and sodium peroxide in equal proportions, a portion of these reagents being spread over the mixture. After heating gently for about 15 minutes, the fusion is completed by heating to dull redness for 5 minutes. The contents of the crucible are extracted with water and rinsed into a 450 c.c. conical flask, treated with the 25-31 c.c. of sulphuric acid (1 : 1), and the volume reduced to 100 c.c. by boiling. One gm. of potassium iodide is now added and the liquid further concentrated to 40 c.c. After removing the last traces of iodine by means of a few drops of dilute sulphurous acid, the green solution is diluted with hot water and saturated with hydrogen sulphide. The arsenious sulphide is collected, washed, dissolved in 20 c.c. of $^N/_2$ sodium hydroxide and treated with 30 c.c. of hydrogen peroxide (20 vols.), the excess of the latter being destroyed by heating. A few drops of phenolphthalein are now added, followed by 11 c.c. of sulphuric acid (1 : 1) and 1 gm. of potassium iodide. The solution is concentrated to 40 c.c., decolorized with a few drops of dilute sulphurous acid, diluted with cold water, neutralized with 2N-sodium hydroxide, and slightly acidulated with sulphuric acid. An 11 per cent. solution of sodium phosphate (compare Washburn, *J. A. C. S.*, 1908, **30**, 31), is then added, and the arsenite solution titrated with iodine and starch in the usual way. The volume of sodium phosphate solution added should be about equal to that of $^N/_{10}$ iodine required in the titration. Compounds containing little or no oxygen require a proportionately larger quantity of sodium peroxide for oxidation. When the arsenic compound contains iodine, sodium iodate is formed on oxidation, and sufficient sulphurous acid must be added to the acidified extract to reduce this salt to iodide.

BARIUM.

Ba = 137·37.

IN a great number of instances the determination of barium is simply the converse of the process for sulphuric acid (*q.v.*), using either a standard solution of sulphuric acid or a neutral sulphate in a known excess, and finding the amount by residual titration.

When barium can be separated as carbonate, the determination is made as on p. 73.

Precipitation as Barium Chromate.—A decinormal solution of dichromate for precipitation purposes must differ from that used for oxidation purposes. In the present case the solution is made by dissolving 7·37 gm. of pure potassium dichromate in water, and diluting to 1 litre.

---

[1] *J. C. S.*, 1909, **95**, 1477.

[2] *Am. Chem. J.*, 1904, **31**, 386.

[3] *Am. J. Sci.*, 1890 (3), **11**, 66.

METHOD OF PROCEDURE: The barium compound, which may contain alkalis, magnesia, strontia, and lime, is dissolved in a good quantity of water, ammonia free from carbonate added, heated to 60° or 70° C., and the standard dichromate added cautiously, with shaking, so long as the yellow precipitate of barium chromate is formed, and until the clear supernatant liquid possesses a faint yellow colour. 1 c.c $^{N}/_{10}$ solution = 0·00687 gm. Ba.

Titration of the Precipitate with Permanganate.—In this case the precipitate of barium chromate is well washed, transferred to a flask, and mixed with an excess of ferrous ammonium sulphate; the amount of iron oxidized by the chromic acid is then determined by residual titration with permanganate; the quantity of iron changed to the ferric state multiplied by the factor 0·8187 = Ba.

Or the barium chromate may be digested with HCl and KI, as mentioned on p. 144. 1 c.c. $/_{10}$ thiosulphate = ·004579 gm. Ba.

$$BaCrO_4 + 2HCl = BaCl_2 + H_2CrO_4$$
$$2H_2CrO_4 + 12HCl + 6KI = 6KCl + 2CrCl_3 + 3I_2$$

METHOD OF PROCEDURE (J. Waddell).[1]—To the solution of the barium salt 30 per cent. ammonium acetate solution is added (10 c.c. to 50 c.c. of a 0·3 per cent. solution of barium chloride) and the barium precipitated by adding 15 c.c. of a 10 per cent. solution of ammonium dichromate (or potassium chromate) to the boiling liquid. The boiling is continued for a minute, and the flask cooled. The precipitate is collected on a Gooch filter and, after thoroughly washing with water, is removed, together with the asbestos, to a beaker, and dissolved in a portion of a mixture of 25 c.c. strong hydrochloric acid and 75 c.c. of cold water. The contents of the beaker are transferred to the original flask with the remainder of the hydrochloric acid and the liquid made up to about 200 c.c. with water. Add 6 gm. potassium iodide, and after ten minutes titrate the liberated iodine rapidly with thiosulphate till near the end-point. Add starch, then thiosulphate cautiously until the blue tint has nearly disappeared. Then add about 10 c.c. of strong hydrochloric acid, warm to about blood-heat to hasten the last stages of the reaction, and complete the titration. Waddell found that 100,000 of wash-water dissolved 0·78 barium chromate, dilute ammonium acetate solution dissolving four times as much.

BISMUTH.

Bi = 208.

THE determination of this metal or its compounds volumetrically has occupied the attention of Pattison Muir, to whom we are indebted for several methods of gaining this end. Two of the best are given here, namely, (1) precipitation of the metal as basic oxalate, and titration with permanganate; (2) precipitation as phosphate with excess of standard sodium phosphate, and titration of that excess by standard uranium acetate.

---

[1] *Analyst*, 1918, **43**, 287.

1. Titration as Oxalate.

Normal bismuth oxalate, produced by adding excess of oxalic acid to a nitric acid solution of the metal, when separated by filtration, and boiled with successive quantities of water three or four times, is transformed into basic oxalate.

METHOD OF PROCEDURE: The solution containing bismuth must be free from hydrochloric acid, as the basic oxalate is readily soluble in that acid. A large excess of nitric acid must also be avoided. Oxalic acid must be added in considerable excess. If the precipitate be thoroughly shaken up with the liquid and the vessel is then set aside, the precipitate quickly settles, and the supernatant liquid may be poured off through a filter in a very short time. If the precipitate be boiled for five or ten minutes with successive quantities of about 50 c.c. of water, it is quickly transformed into the basic salt. So soon as the supernatant liquid ceases to show an acid reaction, the transformation is complete. It is well to employ a solution of permanganate so dilute that at least 50 c.c. are required for the titration ($/_{10}$ strength suffices). The basic oxalate may be dissolved in dilute sulphuric acid in place of hydrochloric; it is more soluble, however, in the latter acid. If the solution contains but little hydrochloric acid, there is no danger of chlorine being evolved during the process of titration.

In applying this process to the determination of bismuth in a solution containing other metals, it is necessary, if the solution contain substances capable of acting upon, or of being acted on by, permanganate, to separate the bismuth from the other metals present. This is easily done by precipitating in a partially neutralized solution with much warm water and a little ammonium chloride. The precipitate must be dissolved in nitric acid, and the liquid boiled down once or twice with addition of the same acid in order to expel all hydrochloric acid, before precipitating as oxalate. The liquid should contain just sufficient nitric acid to prevent precipitation of the basic nitrate before oxalic acid is added, 1 molecule oxalic acid (126·048) corresponds to 1 atom bismuth (208).

1 c.c. $^{N}/_{10}$ permanganate = ·0104 gm. Bi.

A shorter method, based on the same reactions, has been arranged by Muir and Robbs.[1] In this case, however, the double oxalate of potassium and bismuth is the compound obtained, the excess of oxalate of potash being determined residually. Reis[2] has shown that when normal potassium oxalate is added to a solution of bismuth nearly free from mineral acid, but containing acetic acid, a double salt of the formula $Bi_2 (C_2O_4)_3, K_2C_2O_4$ is precipitated. In applying this process for the determination of bismuth in mixtures, it is necessary to separate the metal as oxychloride, and that it should be obtained in solution as nitrate with a small excess of nitric acid. This is done by evaporating off the greater part of the free acid, allowing just sufficient to remain that the bismuth may remain in solution while hot. A large excess of acetic acid is then added, it is made up to a definite measure, and an aliquot portion taken for titration.

---

[1] *J. C. S.*, 1882, **41**, 1.

[2] *Berichte*, 1881, **14**, 1172.

The solution of normal potassium oxalate standardized by permanganate must not be added in great excess It is well, therefore, to deliver it into the bismuth liquid from a burette until the precipitation is apparently complete, then add a few extra c.c., and allow to remain for some time with shaking. It is then filtered through a dry filter, a measured portion taken, and the residual oxalic acid found by permanganate.

For determining bismuth in ores the following method has been worked out by Warwick and Kyle.[1]

One gm. of the finely powdered ore is evaporated to dryness with 5 or 10 c.c. of strong nitric acid, another 5 c.c. of acid and 25 c.c. of water are added, and the whole is diluted to 100 c.c. Five gm. of ammonium oxalate or oxalic acid are introduced, boiled for five minutes, allowed to settle, and the supernatant liquid filtered off. The precipitate is boiled twice with 50 c.c. of water, and the washings are passed through the same paper. With an ordinary ten per cent. ore this treatment should suffice to convert the bismuth oxalate into the basic salt; but if the filtrate is still acid, boiling must be repeated to neutrality. The precipitate on the paper is then dissolved in 2 to 5 c.c. of 1 : 1 HCl, receiving the liquid in the beaker containing the bulk of the basic oxalate; this is warmed till entirely dissolved, and then diluted to 250 c.c. with hot water. The solution is neutralized with ammonia, and the resulting precipitate taken up in 1 : 4 H_2SO_4, adding a few c.c. in excess. Finally the liquid is titrated at between 70° and 100° C. with permanganate. A permanganate solution in which 1 c.c. = 0·010 gm. Fe will be equal to 0·0186 gm. bismuth; by diluting 100 c.c. of this with 86 c.c. of water a solution of permanganate will be obtained, of which 1 c.c should equal 0·010 gm. of bismuth. A permanganate solution 1 c.c. = 0·010 gm. Fe; found = 0·01868 gm. Bi. 100 c.c. permanganate above + 86 c.c. of water; 1 c.c. found = 0·01017 gm. Bi. Lead, iron, copper, zinc, arsenic, and tellurium do not interfere with the process. Care must be taken to avoid using too little or too much nitric acid. Hydrochloric acid must not be used to dissolve the ore. The results are accurate enough for all commercial work, and an analysis occupies little time. The figures quoted show maximum errors of − 0·0032 and + 0·001 gm. in determining 0·5 gm. of bismuth in presence of lead, copper, zinc, iron, and arsenic.

2. Precipitation as Phosphate.

The necessary standard solutions are—

(*a*) Standard sodium phosphate containing 35·8 gm. per litre.

1 c.c. = 0·0071 gm. P_2O_5 or 0·0208 gm. Bi.

(*b*) Standard uranium acetate, corresponding volume for volume with the above, when titrated in the presence of an approximately equal amount of sodium acetate and free acetic acid.

Success depends very much upon identity of conditions, as is explained under Phosphates.

Method of Procedure: The bismuth to be determined must be dissolved in nitric acid; bases other than the alkalis and alkaline earths must be absent. The absence of those acids which interfere with the determination of phosphoric acid by the uranium process (non-volatile, and reducing organic acids, sulphuretted hydrogen, hydriodic acid, etc.) must be assured. As bismuth is readily separated from other metals, with the exception of antimony and tin, by additions of much warm water and a little ammonium chloride to feebly acid solutions, a separation of the bismuth from those other metals which are present should precede the process of determination. If alkalis or alkaline earths be alone present, the separation may be dispensed with. The precipitated bismuth salt is to be washed, dissolved in a little strong nitric acid, and the solution boiled down twice with addition of a little more nitric acid, in order to remove the whole of the hydrochloric acid present.

---

[1] *C. N.*, 1897, **75**, 3.

Such a quantity of a tolerably concentrated solution of sodium acetate is added as shall ensure the neutralization of the nitric acid, and therefore the presence in the liquid of free acetic acid. If a precipitate form, a further addition of acetate must be made. The liquid is heated to boiling; a measured volume of the sodium phosphate solution is run in; the boiling is continued for a few minutes; the liquid is passed through a folded filter, the precipitate being washed repeatedly with hot water; and the excess of phosphoric acid is determined in the filtrate by titration with uranium. If the filtered liquid be received in a measuring flask, which is subsequently filled to the mark with water, and if the inverted uranium method be then employed, the results are exceedingly accurate. This method is especially to be recommended in the determination of somewhat large quantities of bismuth, since it is possible that in such cases a large amount of sodium acetate will have been used, which, as is well known, has a considerably disturbing effect on the reaction of the indicator.

If the bismuth solution contain a large excess of nitric acid, it is better to neutralize nearly with sodium carbonate before adding sodium acetate and titrating.

Fuller details of both the above processes are contained in *J. C. S.*, 1877 (p. 674) and 1878 (p. 70).

BROMINE.

Br = 79·92.

THIS element, or its unoxidized compounds, can be determined in precisely the same way as chlorine by $^{N}/_{10}$ silver solution (p. 146), or by thiocyanate (p. 150), but these methods are seldom of any avail, since the absence of chlorine or its combinations is a necessary condition of accuracy.

Bromine in aqueous solution, or as gas, may be determined by absorption with solution of potassium iodide, in many cases by mere digestion, and in other cases by distillation, in any of the forms of apparatus given on p. 140 *et seq.*, and the operation is carried out precisely as for chlorine (p. 184). 1 eq. I = 1 eq. Br, or

$$\text{I found} \times 0{\cdot}6297 = \text{Br}, (\log.\ \bar{1}{\cdot}79913).$$

A process for the determination of bromine in presence of chlorine is still much wanted in the examination of kelp liquors, etc. Heine[1] uses a colour method in which the bromine is liberated by free chlorine, absorbed by ether, and the colour compared with an ethereal solution of bromine of known strength. Fehling states that with care the process gives fairly accurate results. It is, of course, necessary to have an approximate knowledge of the amount of bromine present in any given solution.

Reimann[2] adopts the following method, which gives tolerably accurate results, but requires skill and practice.

The neutral bromine solution is placed in a stoppered vessel, together with a globule of chloroform about the size of a hazel nut. Chlorine water of known strength is then added cautiously from a burette, protected from bright light, in such a way as to ensure first the liberation of the bromine, which colours the chloroform orange yellow; then more chlorine water is added, until the yellowish white colour of chloride of bromine appears ($KBr + Cl_2 = KCl + BrCl$).

The operation may be assisted by making a weak solution of potassium chromate, of the same colour as a solution of chloride of bromine in chloroform, to serve as a standard of comparison.

The strength of the chlorine water is ascertained by potassium iodide and $^N/_{10}$ thiosulphate. 2 eq. Cl = 1 eq. Br.

In examining mother-liquors containing organic matter, they must be evaporated to dryness in presence of free alkali, ignited, extracted with water; then neutralized with hydrochloric acid before titrating as above.

Cavazzi[3] gives a method which answers well for determining bromine in small quantity, when mixed with large proportions of alkali chlorides. It is based on the fact that, when such a mixture is heated to 100° C. with barium peroxide and sulphuric acid, the whole of the bromine is liberated with a mere trace of chlorine; the bromine so evolved is absorbed in any convenient apparatus, such as fig. 35.

The distillation is carried out in a 350 c.c. flask with double bored stopper; one bore carries an open tube reaching to the bottom of the flask, the other the delivery tube which is connected with the **U** tubes. The first **U** tube is empty; the second contains 20 c.c. of a standard solution of arsenious acid in hydrochloric acid, containing 0·005 gm. As_2O_3 in each c.c., and is connected with an aspirator or water pump. The apparatus is so arranged that the flask and empty **U** tube are immersed in boiling water, the vapours of H_2O_2 are thus decomposed, and the stream regulated by the aspirator.

The reagents used by the author are—

Barium peroxide, containing 63 per cent. BaO_2.

Dilute sulphuric acid 1 : 2.

Arsenious acid dissolved in dilute hydrochloric acid, 5 gm. of pure As_2O_3 per litre.

Standard permanganate, 3·55 gm. per litre.

It was found that the relative strengths of the arsenic and permanganate solutions, when titrated together, diluted, and boiling, were, 18·2 c.c. of the latter to 20 c.c. of the former. Therefore 1 c.c. of permanganate by calculation = 0·00888 gm. Br.

---

[1] *Journ. f. pract. Chem.*, **36**, 184.

[2] *Annal. d. Chem. u. Pharm.*, **115**, 140.

[3] *Gazz. Chim. Ital.*, **13**, 174.

The author found that treating 2 gm. of KCl in the apparatus, without bromine, always gave a faint trace of Cl, so that only 18 c.c. of permanganate were required for the 20 c.c. of arsenic, instead of 18·2 c.c.; and this he regards as a constant for that quantity of material. The examples of analysis with from 0·05 to 0·2 gm. KBr, and all with the addition of 0·2 c.c., are satisfactory.

Norman McCulloch[1] has described a method, devised by himself, for the rapid and accurate determination of bromine, in presence of iodine or chlorine, in any of the ordinary commercial forms or chemical combinations free from oxidizing and reducing agents and metals forming bromides insoluble in hydrochloric acid. The author's explanation of the principles upon which the method is based is complicated and voluminous, and to this the reader is referred. I have not been able to verify the method, but as the author is known to have practical experience, as well as theoretical knowledge, a short summary is given here.

The solutions described by the author are—

Standard permanganate, 3·19 gm. per litre;

Standard potassium iodide, 8·278 per litre.

The solutions should agree volume for volume, but it is preferable to verify them by dissolving 2-3 gm. of iodine in caustic soda, in a 150 c.c. stoppered bottle, adding HCl in good excess, cooling, then adding the permanganate from a burette until nearly colourless. A little chloroform as indicator is then added, and the permanganate cautiously run in, with shaking, until the violet colour of the iodine is discharged, owing to production of ICl, due to the reaction of Cl liberated by the permanganate from HCl. The iodine equivalent of the permanganate is calculated to bromine by the coefficient × 0·6713 and each c.c. permanganate should represent about 0·004 gm. of Br.

The other reagents are:—Chloroform, purified by adding some permanganate, then HCl till the colour is discharged, then a little KI and the I so liberated again discharged with permanganate, the chloroform being finally washed free from all acid;

A 3 per cent. solution of hydrocyanic acid, made by decomposing a solution of pure potassium cyanide with excess of HCl and adding permanganate till a faint pink colour remains. 40 gm. of KCN in 400 c.c. of water with 70 c.c. of HCl will give such a solution. Owing to its poisonous nature great caution must be used in making this solution, and to avoid as much as possible the evolution of hydrocyanic acid the temperature must be kept down by ice or a freezing mixture of nitre and sal ammoniac. If the cyanide contains, as is often the case, some alkali carbonate, this should be removed previously by $BaCl_2$, as otherwise CO_2 will be liberated and a loss of HCN occur. Finally the cool solution is rendered faintly pink with some permanganate;

Solution of manganous chloride, made by dissolving 500 gm. of $MnCl_2, 4H_2O$ in 250 c.c. of warm water. This solution is used to prevent the liberation of free chlorine from the HCl in the analysis.

Method of Procedure: The weighed bromide, containing from 0·05 to 0·15 gm. of Br, is dissolved in 15 c.c. of water in a 150 c.c. stoppered bottle, and about 30 c.c. of the manganese solution added; permanganate is then run in in excess of the required quantity, and the bottle cooled rapidly to 10° C. by ice or a freezing-mixture. When cooled, the bottle is shaken by a rotary motion, and about 15 c.c. of moderately strong HCl slowly added, with motion of the bottle to dissolve the manganic hydroxide, 2·4 c.c. of hydrocyanic solution are then delivered in, the bottle closed and returned to the cooling mixture for about half an hour. The liquid is then titrated with the standard potassium iodide, until nearly decolorized from the decomposition of the manganic chloride, and then slightly coloured from liberation of free I. Lastly, the slight excess of iodide is determined by adding a little chloroform, and the titration finished with permanganate. The bromine is calculated by taking the difference between the amounts of bromine, represented by total permanganate and iodide used. If iodine is present it is, of course, recorded as bromine, and its amount, if required, must be ascertained by some other method capable of its determination in the presence of bromine.

---

[1] *C. N.*, 1889, **60**, 259. See also L. W. Winkler, *Z. angew. C.*, 1915, **28**, 477, 494.

The author gives several very good results obtained with pure sodium bromide.

For the determination of bromine in mineral waters and brines, Baughman and Skinner[1] have developed a method proposed by Wyss. The solid residue of chlorides and bromides, from which the iodides have previously been removed, is treated with a concentrated solution of chromic acid at the ordinary temperature. Bromine is liberated with only a trace of chlorine, most of which remains in solution as chromyl chloride. At the same time a little chlorobromide is formed, and is removed with the bromine by aspirating. The bromine is absorbed in potassium iodide solution.

CADMIUM.

Cd = 112·4.

This metal may be determined, as may many others, by precipitating as sulphide and decomposing the sulphide with a ferric salt, the iron being reduced to the ferrous state in proportion to the amount of sulphide present.

Follenius has found that when cadmium is precipitated as sulphide in acid liquids the precipitate is apt to be contaminated to a small extent with salts other than sulphide. The separation as sulphide is best made by passing H_2S into the hot liquid which contains the cadmium, and which should be acidified with 10 per cent. of concentrated sulphuric acid by volume. From hydrochloric acid solutions the metal is only completely separated by H_2S when the hot solution contains not more than 5 per cent. of acid of sp. gr. 1·11, or 14 per cent. if the liquid is cold.

Ferric chloride is to be preferred for the decomposition of the cadmium sulphide, and the titration is carried out precisely as in the case of Zinc (q.v.).

P. von Berg[2] gives a good technical process for the determination of either cadmium or zinc as sulphide, by means of iodine as follows :—

---

[1] *J. Ind. and Eng. Chem.*, 1919, 11, 954.

[2] *Z. a. C.*, 1887, 26, 23.

METHOD OF PROCEDURE: The washed sulphide of zinc or cadmium is allowed to drain upon the filter, and then transferred, together with the filter, to a stoppered flask containing 800 c.c. of water deprived of air by boiling and the passage of carbonic acid gas. The whole is well shaken in order to break up the precipitate and bring it into the most finely divided condition possible, so that the sulphide may not be protected from the action of the iodine by separated sulphur. A moderate quantity of hydrochloric acid is added, there being no necessity to entirely dissolve the sulphide, and then an excess of iodine solution of known strength. The residual free iodine is then titrated with thiosulphate without loss of time. The whole operation, from the transference of the sulphide to the flask to the final titration, occupies about five minutes, and gives results varying between 98·8 and 100·2 per cent. The reaction proceeds according to the equation, $ZnS + 2HCl + I_2 = ZnCl_2 + 2HI + S$.

CALCIUM.

$\dot{Ca} - 40·07$.

1 c.c. N/10 permanganate = 0·0028035 gm. CaO
" " = 0·0050035 gm. $CaCO_3$
" " = 0·0086086 gm. $CaSo_4, 2H_2O$
" normal oxalic acid = 0·02805 gm. CaO
Cryst. oxalic acid × 0·444 = CaO
Ferrous ammonium sulphate × 0·07143 = CaO

THE determination of calcium alkalimetrically has already been described (p. 73), but that method is of limited application, unless calcium oxalate, in which form Ca is generally separated from other bases, be converted into carbonate or oxide by ignition, and thus determined with normal nitric acid and alkali. This and the following method by Hempel are as exact in their results as the determination by weight; and where a series of determinations have to be made, the method is very convenient.

Titration with Permanganate.—The readiness with which calcium can be separated as oxalate facilitates the use of this method, so that it can be applied successfully in a great variety of instances. It is not necessary here to enter into detail as to the method of precipitation; except to say that it may take place in either ammoniacal or weak acetic acid solution, and that it is absolutely necessary to remove all excess of ammonium oxalate from the precipitate by washing with warm water previous to titration.

METHOD OF PROCEDURE: When the clean precipitate is obtained, a hole is made in the filter, and the bulk of the precipitate is washed through the funnel into a flask, the filter is then treated with small quantities of hot dilute sulphuric acid, and again washed into the flask. Hydrochloric acid in moderate quantity may safely be used for the solution of the oxalate, since there is not the danger of liberating free chlorine which exists in the case of iron (Fleischer, *Titrirmethode*, p. 76), but sulphuric is better.

When the precipitate is completely dissolved, the solution is freely diluted with water, and further acidified with sulphuric acid, warmed to

60° or 70°, and the standard permanganate cautiously delivered into the liquid with constant agitation until a faint permanent pink tinge is produced, precisely as in the case of standardizing permanganate with oxalic acid (p. 130).

PROCEDURE FOR LIME IN BLAST FURNACE SLAGS: Place about 1 gm. of the very finely-ground slag into a beaker, cover with water, and boil gently, then add gradually strong HCl until the whole is dissolved, including SiO_2. Dilute the liquid, nearly neutralize with ammonia, and add a solution of ammonium acetate. The silica and alumina form a flocculent precipitate which is easily washed on a filter. The filtrate and washings are concentrated somewhat, and the CaO precipitated with ammonium oxalate and ammonia; the precipitate is dissolved as before described in hot dilute sulphuric acid, and titrated with permanganate. If much manganese is present, the calcium oxalate must be re-dissolved and re-precipitated before the titration is made.

In all cases where a clean oxalate precipitate can be obtained, such as mineral waters, manures, etc., very exact results are obtainable; in fact, quite as accurate as by the gravimetric method. Ample testimony on this point is given by Fresenius, Mohr, Hempel, and others. When much iron, alumina, magnesia, etc., is present, it will be preferable to re-precipitate the oxalate, so as to free it from adhering contaminations previous to titration.

Indirect Titration.—In the case of calcium salts soluble in water and of tolerably pure nature, the determination by permanganate can be made by adding to the solution a measured excess of normal oxalic acid, then ammonia in slight excess, and heating to boiling, so as rapidly to separate the precipitate. The mixture is then cooled, diluted to a measured volume, filtered through a dry filter, and an aliquot portion titrated with permanganate, after acidifying with sulphuric acid as usual. A great variety of calcium salts may be converted into oxalates by a short or long treatment with oxalic acid or ammonium oxalate, including calcium sulphate, phosphate, tartrate, citrate, etc.

CERIUM.

Ce = 140·25.

Stolba[1] states that the moist cerium oxalate may be titrated precisely as in the case of calcium oxalate with permanganate, and with accurate results. No examples or details, however, are given. It is probable that it is only correct in the case of the pure substance.

This method has, however, been examined by P. E. Browning and A. Lynch,[2] who prepared the oxalate from pure cerium chloride by ammonium oxalate. Definite volumes of the cerium solution, the exact strength of which was known (from 0·1 to 0·2 gm. of $CeCl_3$), were used for precipitation at a moderate temperature, some trials being made on neutral portions and some on portions slightly acid with HCl (in which case about 1 gm. of manganous sulphate was used). The precipitate, after being carefully washed, was dissolved in about 10 c.c. of hot dilute H_2SO_4, and then made up to about 500 c.c. with hot water at about 80° C. when the titration with permanganate was immediately made. The results obtained were, both in the neutral and acid solutions, very near the amounts of cerium taken.

---

[1] *Z. a. C.*, 1880, **19**, 194.

[2] *Amer. Journ. Science*, **8**, No. 48.

Bunsen's method, originated many years ago, showed that the oxide of cerium obtained by ignition of the oxalate might be determined volumetrically by dissolving it in strong HCl with a few crystals of KI in a small sealed flask, which was heated on a water-bath till the oxide was dissolved and the free iodine liberated. The iodine was then titrated with thiosulphate in the usual way and the amount of cerium calculated therefrom.

$$1 \text{ c.c. } {}^{N}/_{10} \text{ thiosulphate} = 0{\cdot}017225 \text{ gm. } CeO_2.$$

A modification of this method was adopted with satisfactory results by Browning, Hanford, and Hall, as follows:—

METHOD OF PROCEDURE: Weighed portions of the pure cerium dioxide, about 0·1 to 0·15 gm., were placed in small glass-stoppered bottles of about 100 c.c. capacity, together with 1 gm. of potassium iodide free from iodate and a few drops of water to dissolve the iodide. A current of CO_2 was passed into the bottle for about five minutes to expel the air, 10 c.c. of pure strong HCl were added, the stopper inserted, and the bottle heated gently upon a steam radiator for about one hour, until the dioxide dissolved completely and the iodine was set free. After cooling the bottle, to prevent loss of iodine upon removing the stopper, the contents were carefully washed into about 400 c.c. of water, and titrated with ${}^{N}/_{10}$ sodium thiosulphate to determine the amount of iodine liberated according to the reaction—

$$2CeO_2 + 8HCl + 2KI = 2CeCl_3 + 2KCl + 4H_2O + I_2.$$

A few blank determinations were carried through in the bottles without the cerium dioxide to determine the amount of iodine set free under these conditions. The amount obtained was uniformly equal to 0·04 c.c. of the ${}^{N}/_{10}$ thiosulphate solution, which was taken as the correction and applied to all the determinations.

Determination in the Presence of other Rare Earths.—G. von Knorre.[1] This is based on the fact that the yellow ceric salts are reduced by hydrogen peroxide in the presence of free acid to colourless cerous salts, as in the equation:

$$2Ce(SO_4)_2 + H_2O_2 = Ce_2(SO_4)_3 + H_2SO_4 + O_2.$$

The cold solution of the ceric salt is mixed with an excess of a dilute solution of hydrogen peroxide, of which the strength is known, and when all colour has disappeared the excess of peroxide is titrated back with permanganate.

If the permanganate be standardized on iron, the amount of cerium present may be expressed in terms of iron, 55·84 parts of the latter being equivalent to 140·25 parts of cerium. It is advisable to use a dilute solution of permanganate (not more than 2 gm. of $KMnO_4$ per litre).

Notwithstanding Rose's statement that permanganate is slowly decolorized by a solution of cerous sulphate, the author finds that the end-reaction can be readily recognised. With a freshly-prepared acidified solution of a ceric salt the reduction takes place instantaneously, but if the solution has been exposed to the air for some time, as long as fifteen minutes may be necessary for complete decolorization. The results obtained, however, in both cases are identical. By boiling an old solution after the addition of sulphuric acid, and cooling before adding the hydrogen peroxide, the rate of reduction is accelerated, and the reaction takes place almost as rapidly as in a freshly-prepared solution.

---

[1] *Z. a. C.*, 1897, **36**, 685-688.

Either sulphuric or nitric acid may be used, but it is essential that the acidification shall take place before the addition of the hydrogen peroxide, since otherwise by-reactions occur and the results are too high.

A method of Gibbs[1] is modified by Job[2] as follows:—

A known volume of the cerium solution is treated in the cold with peroxide of lead, and a large excess of concentrated nitric acid, in order to oxidize any cerous salts present, then the mixture is agitated, filtered, and the filtrate titrated with dilute hydrogen peroxide. The determination of cerium by this method may be carried out equally well in presence of thorium, lanthanum, and didymium, and should thus be of great use in directly determining cerium in the crude oxalates from monazite sand.

CHLORINE.

Cl = 35·46.

1 c.c. $/_{10}$ silver nitrate = 0·003546 gm. Cl.
,, ,, = 0·005846 gm. NaCl.

THE powerful affinity existing between chlorine and silver in solution, and the ready precipitation of the resulting chloride, seem to have led to the earliest important volumetric process in existence, viz., the assay of silver by the wet method of Gay-Lussac. The details of the process are more particularly described under the article relating to the assay of Silver (q.v.); the determination of chlorine is just the converse of the process there described, and the same precautions, and to a certain extent the same apparatus, are required.

The solutions required, however, are systematic, and for exactness and convenient dilution are of decinormal strength as described on p. 146. In many cases it is advisable to possess also centinormal solutions, made by diluting 100 c.c. of $/_{10}$ solution to 1 litre.

1. Direct Precipitation with $/_{10}$ Silver Nitrate (Gay-Lussac).

Very weak solutions of chlorides, such as good drinking waters, are not easily examined for chlorine by direct precipitation, unless they are considerably concentrated by evaporation previous to treatment, owing to the fact that, unless a tolerable quantity of chloride can be formed, it will not collect together and separate so as to leave the liquid clear enough to tell whether on the addition of fresh silver, a distinct formation of chloride occurs. The best effects are produced when the mixture contains chlorine equal to from 1½ to 2 gm. of salt per 100 c.c. Should the proportion be much less than this, the difficulty of precipitation may be overcome by adding a quantity of freshly precipitated chloride, made by mixing equal volumes of $^{N}/_{10}$ salt and silver solutions, shaking vigorously, pouring off the clear liquid, and adding the chloride to the mixture under titration. The best vessel to use for the trial is a well stoppered round white bottle, holding from 100 to 150 c.c., and fitting into a paper case, so as to prevent access of strong light during the titration. Supposing, for instance, a neutral solution of potassium chloride requires titration, 20 or 30 c.c. are measured into the shaking bottle, a few drops of strong nitric acid added (free acid must always be present in direct precipitation), and a round number of c.c. of silver solution added from the burette. The bottle is placed in its case (or may be enveloped in a dark cloth) and vigorously shaken for half a minute, then uncovered, and gently tapped upon a table or book, so as to start the chloride downward from the surface of the liquid where it often swims. A quick clarification indicates excess of silver. The nearer the point of exact counterbalance the more difficult to obtain a clear solution by shaking, but a little practice soon accustoms the eye to distinguish the faintest precipitate.

---

[1] *Z. a. C.*, 1864, 3, 395.

[2] *Compt. Rend.*, 1899, p. 101.

In case of overstepping the balance in any trial, it is only necessary to add to the liquid under titration a definite volume of $^N/_{10}$ salt solution, and finish the titration in the same liquid, deducting, of course, the same number of c.c. of silver as has been added of salt solution.

Fuller details and precautions are given under Silver.

2. Precipitation by $^N/_{10}$ Silver in Neutral Solution with Chromate Indicator (see p. 147).

3. Titration with $^N/_{10}$ Silver and Thiocyanate (see p. 150).

This method gives very accurate results if, after the chlorine is precipitated with excess of $^N/_{10}$ silver, the silver chloride is filtered off, washed well, and the filtrate and washings titrated with $^N/_{10}$ thiocyanate for the excess of silver.

Method of Procedure: The material to be titrated, such as water residues, beer ash, or other substances in which the chlorine is to be determined, being brought into clear solution, a known volume of $^N/_{10}$ silver in excess is added, the mixture having been previously acidified with nitric acid; the mixture is well stirred, and the supernatant liquid filtered off through a small filter, the chloride well washed, and to the filtrate and washings 5 c.c. of ferric indicator (p. 151) and the same volume of nitric acid (p. 152) are added. The flask is then brought under the thiocyanate burette, and the solution delivered in with a constant gentle movement of the liquid until a permanent light-brown colour appears. If the silver chloride is not removed from the liquid previous to titration a serious error may result, owing to the ready solubility of the chloride in the thiocyanate solution.

4. By Distillation and Titration with Thiosulphate or Arsenite.

In cases where chlorine is evolved directly in the gaseous form or as the representative of some other body (see p. 140), a very useful absorption apparatus is shown in fig. 35. The little flask *a* is used as a distilling vessel, connected with the bulb tubes by an india-rubber joint;[1] the stoppers for the tubes are also of the same material, the whole of which should be cleansed from sulphur by boiling in weak alkali. A fragment of solid magnesite may with advantage be added to the acid liquid in the distilling flask; in all other respects the process is conducted exactly as is described on p. 140 *et seq.*

This apparatus is equally well adapted to the absorption of ammonia or other gases, and possesses the great recommendation that there is scarcely a possibility of regurgitation.

Mohr's apparatus (fig. 36), is also serviceable for this method.

CHLORINE GAS AND BLEACHING COMPOUNDS.

1 c.c. $^N/_{10}$ sodium arsenite or thiosulphate solution = 0·003546 gm. Cl.
1 litre of chlorine at 0° C., and 760 mm., weighs 3·2191 gm.

CHLORINE water may be titrated with thiosulphate by adding a measured quantity of it to a solution of potassium iodide, then delivering the thiosulphate from a burette till the colour of the free iodine has disappeared; or by using an excess of the reducing agent, then starch, and titrating residually with $^N/_{10}$ iodine. When arsenious solution is used for titration, the chlorine water is delivered into a solution of sodium bicarbonate, excess of arsenious solution added, then starch and $^N/_{10}$ iodine till the colour appears, or iodized starch-paper may be used.

Bleaching Powder.—This important substance, which is also called *chloride of lime*, is made by the action of chlorine gas on slaked lime. Its composition appears to be best represented by the formula $Ca(OCl)Cl$,[2] which is due to Odling. When treated with water, it is resolved into calcium chloride and hypochlorite, thus:—

$$2Ca(OCl)Cl = CaCl_2 + Ca(OCl)_2.$$

The calcium hypochlorite constitutes the bleaching agent.

The technical analysis is confined to the determination of the "available" or "bleaching" chlorine, which in England and America is always expressed as percentage by weight on the bleaching powder. In France, however, its strength is given in Gay-Lussac degrees, which indicate the number of litres of chlorine gas, at 0° C. and 760 mm., capable of being evolved from one kilogram of bleaching powder.

100 French Degrees = 31·78 per cent. chlorine.

1. Titration by Arsenious Solution (Penot).

The commercial valuation of bleaching powder (or "bleach") is carried out as follows:—

The sample is well and quickly mixed, and 7·092 gm. weighed, put into a mortar, a little water added, and the mixture rubbed to a smooth cream; more water is then stirred in with the pestle, allowed to settle a little while, then poured off into a litre flask; the sediment again rubbed with water, poured off, and so on repeatedly, until the whole of the sample has been conveyed into the flask without loss, and the mortar washed quite clean. The flask is then filled to the mark with water, well shaken, and 50 c.c. of the milky liquid (= 0·3546 gm. bleaching powder) pipetted into a beaker, and the $^{N}/_{10}$ arsenious solution delivered in from a burette until a drop of the mixture taken out with a glass rod and brought in contact with iodized starch-paper (p. 145) gives no blue stain.

---

[1] India-rubber and especially vulcanized rubber is open to some objection in these analyses, and apparatus is now readily to be had with glass connections.

[2] Calcium chloro-hypochlorite.

Mohr's Modification.—The starch-paper may be dispensed with by adding arsenious solution in excess, then starch, and titrating residually with $^{N}/_{10}$ iodine till the blue colour appears. The number of c.c. of arsenite used gives percentage of available chlorine (35 per cent. available chlorine is a common guarantee).

2. Bunsen's Method.

10 or 20 c.c. of the chloride of lime solution, prepared as above, are measured into a beaker, and an excess of solution of potassium iodide added; the mixture is then diluted somewhat, acidified with acetic acid, and the liberated iodine titrated with $^{N}/_{10}$ thiosulphate and starch; 1 eq. iodine so found represents 1 eq. chlorine.

The presence of chlorate does not affect the result when acetic acid is used. If it be desired to determine the amount of chlorate in bleach, the following method has been devised by R. Fresenius. It depends on the fact that hypochlorites are decomposed by lead acetate with formation of lead peroxide, whilst the chlorate which may be present is unaffected.

METHOD OF PROCEDURE: 20 gm. of bleaching powder are ground up with water in repeated quantities and made up to a litre; after settling, 50 c.c. (= 1 gm. of bleach) are filtered off through a dry filter, put into a flask, and mixed with a solution of lead acetate in some excess. There is formed at first a white precipitate of lead chloride and lead hydroxide; these being acted on by the hypochlorite become first yellow, then brown, with liberation of chlorine and passing into lead peroxide. After the precipitate has settled, more lead solution is added, to make sure that the conversion is complete. The mixture is allowed to stand in the open flask, with frequent shaking, till all smell of chlorine has disappeared, which occurs in from eight to ten hours. The precipitate is then filtered off and washed till the wash-water is free from acid. The washings are evaporated somewhat, added to the filtrate, and the whole mixed with sodium carbonate in slight excess, to precipitate the lead and lime as carbonates; these are well washed, the filtrate and washings, which contain the chlorate as the sodium salt, evaporated nearly to dryness, then transferred to either a Fresenius or Mohr apparatus (fig. 35 or 36) and distilled with HCl as directed on p. 140 *et seq.* 1 eq. : I = Cl_2O_5.

Mixtures of Chlorides, Hypochlorites, and Chlorates.—It is known that chlorine acting upon alkali and alkaline-earthy hydrates gives rise to chlorides, and at the same time to chlorates, or to hypochlorites, according as the temperature and the concentration are higher or lower. Under average conditions the three kinds of salts are formed simultaneously.

A mixture of the same salts is produced if solutions of sodium chloride are submitted to electrolysis, according to the processes recently used for the manufacture of free chlorine and of caustic soda, or of chlorates, or hypochlorites.

In these various cases it is of great industrial importance to determine easily the proportion of each of the salts present.

For the analysis of such a mixture of salts, the subjoined method is recommended as at once expeditious and accurate. All the determinations are performed successively upon the same solution.[1]

METHOD OF PROCEDURE: 1. The mixture of hypochlorite, chlorate, and chloride is poured into a beaker. There is then run into it from a burette a standard solution of alkali arsenite until the hypochlorite is completely reduced. To find the exact moment when the reduction is completed, a drop of the liquid is placed upon a porcelain plate in contact with a drop of solution of potassium iodide and starch.

On the mixture of the two drops there appears a blue colour as long as there remains any hypochlorite not reduced. As soon as the mixture ceases to become coloured, the volume of the arsenite liquid is noted, and the proportion of hypochlorite or hypochlorous acid which has transformed it into arsenic acid is obtained; or consequently, that of the corresponding chlorine.

$$As_2O_3 + CaCl_2O_2 = As_2O_5 + CaCl_2.$$

or

$$As_2O_3 + 2NaClO = As_2O_5 + 2NaCl.$$

2. The liquid (which now contains merely chlorate and chloride) is slightly acidified with sulphuric acid, and a quantity of ammonium-ferrous sulphate added, at least twenty times as much as the chlorate supposed to be present. Heat to about 100°, adding in small successive quantities 5 c.c. of sulphuric acid diluted with 15 c.c. of water. It is best to use a tap-funnel, letting the acid fall in drop by drop. After having stoppered the vessel, to avoid contact of air, it is allowed to cool for a short time, and the excess of ferrous salt is then titrated with permanganate. As the quantity of ferrous salt which was introduced is known, by difference the quantity which has been peroxidized at the expense of the chlorate reduced to the state of chloride is found

$$NaClO_3 + 6FeO = NaCl + Fe_2O_3.$$

It is thus easy to calculate the proportion of chlorate or of chloric acid, or the corresponding quantity of chlorine.

3. The total chlorine, which is now present entirely in the state of chloride, is determined as follows:—The rose tint produced by the permanganate is removed by adding a trace of ferrous sulphate. Then add a measured volume of standard silver nitrate, more than enough to precipitate all the chlorine, and determine the excess of the silver salt by means of standard thiocyanate (p. 151). The ferric salt previously formed by the peroxidation of the ferrous salt serves as an indicator, by producing a permanent red coloration as soon as there is no more silver salt to precipitate. The arsenic acid produced in the first operation does not interfere in the least.

---

[1] A. Carnot, *Compt. Rend.*, 1896, **122**, 449.

In order to avoid the use of too large a quantity of silver nitrate, which would be necessary on account of the large proportion of chlorine to be precipitated, an aliquot part of the solution may be taken.

The chlorine found in the form of chloride in the original liquid is easily calculated by deducting from the total chlorine just determined the two quantities already found in the state of hypochlorite and of chlorate.

The three operations succeed each other without interruption, and without separate preparation, and are completed in a short time.

In a number of experiments with mixtures, the discrepancies found between the experimental results and the calculated numbers rarely reached 1 mgm. when operating upon from 250 to 500 mgm.

Mixtures of Chlorides, Chlorates, and Perchlorates.—A. Carnot.[1] Perchlorates are found with chlorides and chlorates in the products of the calcination of chlorates. Hypochlorites are only produced in the cold or by wet methods; but in such cases no perchlorates are formed, nor can the latter be reduced by the usual reagents in solution, direct application of heat being necessary to accomplish this result.

In analysing such mixtures, the chlorides and chlorates are determined first by titrating one portion of the solution for the chlorides by Volhard's method, and the other part for the total chlorine after reduction of the chlorates by the aid of ferrous sulphate; or, as an alternative method, both titrations can be performed on the same liquid, the chlorides first—with sodium arsenate as indicator in preference to potassium chromate, which would interfere with the subsequent reaction, and then the total chlorine after reduction of the chlorates.

The perchlorates are determined by heating the powdered substance, mixed with four or five times its weight of purified quartz-sand, in a platinum crucible, the mixture being covered by a layer of the same sand 1 or 2 cm. deep. The bottom of the crucible is kept at a red heat for about twenty to thirty minutes, and this is sufficient completely to reduce the chlorates and perchlorates, volatilization of the chloride being prevented by the condensing effect of the upper layer of sand. An aqueous solution is then made, the total chlorides titrated as before, and the perchlorate found by difference.

Determination of Perchlorate in Chili Saltpetre.—Ahrens and Hett.[2] 20 gm. of the powdered sample are introduced into a flat 200 c.c. platinum dish, moistened with 2-3 c.c. of cold saturated caustic soda, 1 gm. of pure manganese dioxide added, and the whole evaporated to dryness; the dish is then covered and heated to redness. When cold, the fused mass is treated with 100 c.c. of hot water, allowed to cool, and then made up to 250 c.c.; 50 c.c. of the filtrate are acidified with 10-15 c.c. of nitric acid of sp. gr. 1·20, and a solution of permanganate is added drop by drop until the colour is permanent for a minute, showing that all the nitrous acid has been oxidized. The chlorine is then determined by Volhard's process, and the difference between the amounts of chlorine found before and after fusion is calculated into perchlorate. Iodides present in the sample do not interfere, as they are oxidized to iodates by the permanganate.

The Iodimetric Determination of Chloric and Nitric Acids.—The following methods by McGowan[3] depend on the principle that when a fairly concentrated solution of a nitrate or chlorate is warmed with an excess of pure, strong hydrochloric acid, a nitrate is completely decomposed, and the production of nitrosyl chloride and chlorine is quantitative, the reaction being

---

[1] *Compt. Rend.*, 1896, **122**, 452.

[2] *Chem. Centr.*, 1898, **2**, 558.

[3] *J. C. S.*, **59**, 530 and *J. C. S.*, 1892, **61**, 87.

$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O.$$

If the operation is conducted in an atmosphere of carbonic acid, and the escaping gases are passed through a solution of potassium iodide, an amount of iodine is liberated exactly equivalent to the whole of the chlorine presents (free and combined), nitric oxide escaping. 1 mol. of nitric acid thus yields 3 atoms of chlorine or iodine. The iodine can then be titrated in the usual manner with thiosulphate. With chlorates only chlorine is evolved. De Koninck and Nihoul[1] give details of a process depending upon the same principle.

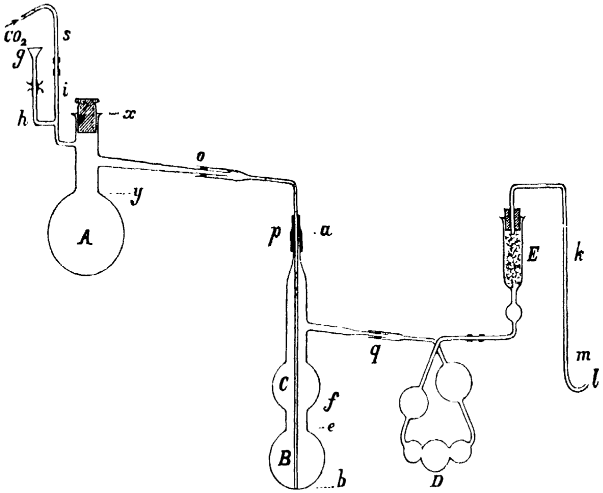

Fig. 38.

Method of Procedure for Nitrates: It is, of course, absolutely essential that air should be completely excluded from the apparatus as, if any were present, the escaping nitric oxide would be re-oxidized to nitrogen trioxide or tetroxide, and this would in its turn liberate a further quantity of iodine from the iodine solution.

The apparatus required is very simple, and can readily be made by anyone moderately expert at glass-blowing. The main point to be attended to is to have no corks or rubber stoppers, etc., for the escaping chlorine to act upon. Fig. 38 is a sketch of the apparatus. The condensing arrangement for the chlorine does its work perfectly, and may therefore be used with advantage, not only for this, but also for other similar methods in which iodine is set free. The measurements given are those of the apparatus as used by the author.

A is a small, round-bottomed flask, into the neck of which a glass stopper, *x*,

[1] *Zeit. für angew. Chem.*, 15th August, 1890.

is accurately ground (with fine emery and oil). The capacity of the bulb is about 46 c.c., and the length of the neck, from *x* to *y*, 90 mm. The first condenser is a simple tube, slightly enlarged at the foot into two small bulbs. The length from *a* to *b* is 300 mm., from *b* to *e* 180 mm., and from *e* to *f* 30 mm. The capacity of the bulb *B* is 25 c.c., and the total capacity of the two bulbs and tube, up to the top of *C*, 41 c.c. This condenser is immersed, up to the level of *e*, in a beaker of water. *D* is a Geissler bulb apparatus, and *E* a chloride of calcium tube, filled with broken glass, which acts as a tower, *g* is a small funnel, attached by rubber and lip to the branch tube *h*. Between the tube *i* and the wash-bottle for the carbonic acid is placed a short piece of glass tubing, *s*, containing a strip of filter-paper, slightly moistened with iodide of starch solution. This tube *s* is really hardly necessary, as no chlorine escapes backwards if a moderate current of carbonic acid is kept passing, but it serves as a check. The joints *p* and *q* are of narrow rubber tubing. The joint *o* is made by grinding one tube into the other. *k* is the outlet tube.

The operation is performed in the following manner:—The evolution flask is washed and thoroughly dried, and the nitrate (say about 0·25 gm. of potassium nitrate) is dropped into it from the weighing tube. 1 to 2 c.c. of water are now added, and the bulb is gently warmed, so as to bring the nitrate into solution, after which the stopper of the flask is firmly inserted into it. About 15 c.c. of a solution of potassium iodide (1 in 4) are run into the first condensing tube, any iodide adhering to the upper portion of the tube being washed down with a little water, and 5 c.c. of the same solution, mixed with 8 to 10 c.c. of water, are sucked into the Geissler bulbs, whilst the glass in tower *E* is also thoroughly moistened with the iodide. The Geissler bulbs should be so arranged that gas only bubbles through the last of them, the liquid in the others remaining quiescent.

All the joints having been made tight, the CO_2 is turned on briskly, and passed through the apparatus until a small tubeful collected at *l*, over caustic potash solution, shows that no appreciable amount of air is left in it. The small outlet tube *l* is now replaced by a chloride of calcium tube, filled with broken glass which has been moistened with the above iodide solution, and closed by a cork through which an outlet tube passes, the object of this "trap" tube being to prevent any air getting back into the apparatus; and the brisk current of CO_2 is continued for a minute or two longer, so as practically to expel all the air from this last tube. The stream of gas is now stopped for an instant, and about 15 c.c. of pure concentrated hydrochloric acid, free from chlorine, run into *A* through the funnel *g* (into the tube of which it is well to have run a few drops of water before beginning to expel the air from the apparatus), and *A* is shaken so as to mix its contents thoroughly. A slow current of CO_2 is now turned on again (1 to 2 bubbles through the wash-bottle per second), and *A* is gently warmed over a burner. It is a distinct advantage that the reaction does not begin until the mixed solutions are warmed, when the liquid becomes orange-coloured, the colour again disappearing after the nitrosyl chloride and chlorine have been expelled. The warming should be very gentle at first, in order to make sure of the conversion of all the nitric acid, and also because the first escaping vapours are relatively very rich in chlorine; after which the liquid in *A* is briskly boiled. A very little practice enables the operator to judge as to the proper rate of warming. When the volume of liquid in *A* has been reduced to about 7 c.c. (by which time it is again colourless), the stream of CO_2 is slightly quickened, and the apparatus allowed to cool down a little. The burner is now set aside for a few minutes, and 2 c.c., or so, more of hydrochloric acid previously warmed in a test-tube, run in gently through *g*; there is no fear either of the iodide solution running back, or of any bubbles of air escaping through *y*, if this is done carefully. This is a precautionary measure, in case a trace of the liberated chlorine might have lodged in the comparatively cool liquid in tube *h*. The CO_2 is once more turned on slowly, and the liquid in *A* is boiled again until it is reduced to about 5 c.c. It is now only necessary to allow the apparatus to cool down, passing CO_2 all the time, after which the contents of the condensers are transferred to a flask and titrated with thiosulphate. At the end of a properly conducted experiment, the glass in the upper part of tower *E* should be quite colourless, and there should only be a mere trace of iodine showing in the lower part of the tower, while the liquid in the last bulb of the Geissler apparatus ought to be only pale yellow. During the operation the stopper of *A* and the various joints can be tested for tightness from time to time by means of a piece of iodide of starch paper, and, before disjointing, it is well to test the escaping gas (say, at *m*) in the same way, to make sure that all nitric oxide has been thoroughly expelled.

Example : 0·2627 gm. of pure KNO_3 was taken. The liberated iodine required 38·55 c.c. of thiosulphate (of which 1 c.c. = 0 006805 gm. KNO_3) for conversion. This gave 0·2623 gm. nitrate found, or 99·86 per cent.

Method of Procedure for Chlorates : The apparatus employed is the same as for nitrates, but since it is unnecessary in this determination previously to expel the air present by a current of CO_2, those tubes which come after the tower *E* are dispensed with. The details of the operation are also practically the same as in the case of a nitrate, only simpler. Comparatively dilute hydrochloric acid may be employed, and the CO_2 is required merely to ensure a regular passage of the vapours through the iodine solution, and to prevent any chlorine escaping backwards. This is tested, as before, by the small piece of iodide of starch paper in tube *s*, which should be so placed as never to get warm.

The chlorate is weighed out into the dry evolution flask *A*, then dissolved in 8 to 10 c.c. of water, and, after all the necessary connections have been made, 8 to 10 c.c. of pure concentrated hydrochloric acid are run in through the funnel *g*. Since the reaction begins in the cold, the CO_2 must be turned on immediately, and kept passing at the rate of about four bubbles per second. Care should be taken to heat very gently at first, until the bulk of the chlorine has come over, after which the lamp flame may be gradually turned up and the liquid boiled, exactly as in the case of the nitrate; this ensures that no chlorine escapes backwards. And, as before, after all the chlorine has been apparently driven out, and the solution has become colourless, a second quantity of warm hydrochloric acid (1 in 2) is run in, and the boiling repeated for a few minutes.

Chlorates, Iodates, and Bromates.

Cl_2O_5 = 150·92. I_2O_5 = 333·84. Br_2O_5 = 239·84. The compounds of chloric, iodic, and bromic anhydrides may all be determined by distillation or digestion with excess of hydrochloric acid; with chlorates the quantity of acid must be considerably in excess.

In each case 1 eq. of the respective anhydrides taken as monobasic, or their compounds, liberates 6 eq. of chlorine, and consequently 6 eq. of iodine when decomposed in the digestion flask. In the case of distillation, however, iodic and bromic acids only set free 4 eq. iodine, while iodous and bromous chlorides remain in the retort. In both these cases digestion is preferable to distillation.

Example: 0·2043 gm. pure potassium chlorate, equal to the sixth part of $\frac{1}{100}$ eq., was decomposed by digestion with potassium iodide and strong hydrochloric acid in the bottle shown in fig. 37. After the reaction was complete and the bottle cold, the stopper was removed and the contents washed out into a beaker, starch added, and 103 c.c. $^{N}/_{10}$ thiosulphate delivered in from the burette; then again 23·2 c.c. of $^{N}/_{100}$ iodine solution, to reproduce the blue colour; this latter was therefore equal to 2·32 c.c. $^{N}/_{10}$ iodine, which deducted from the 103 c.c. thiosulphate gave 100·68 c.c., which multiplied by the factor 0·002043, gave 0·2056 gm., instead of 0·2043 gm.

CHROMIUM.

Cr = 52.

1. Reduction by Iron.

THE determination of chromates is very simply and successfully performed by the aid of ferrous sulphate, being the converse of the process devised by Penny for the determination of iron (see p. 132).

METHOD OF PROCEDURE: A very small beaker or other convenient vessel is partly or wholly filled, as may be requisite, with perfectly dry and granular ferrous ammonium sulphate; the exact weight then taken and noted. The chromium compound is brought into solution, not too dilute, acidified with sulphuric acid, and small quantities of the iron salt added from time to time with a dry spoon, taking care that none is spilled, and stirring with a glass rod, until the mixture becomes green and the iron is in excess, best shown by a small drop being brought in contact with a drop of potassium ferricyanide, when, if a blue colour appears at the point of contact, the iron is in excess. It is necessary to determine this excess, which is most conveniently done by $^{N}/_{10}$ dichromate being added until the blue colour produced by contact with the indicator disappears. The vessel containing the iron salt is again weighed, the loss noted; the quantity of the salt represented by the $^{N}/_{10}$ dichromate deducted from it, and the remainder multiplied by the factor required by the substance sought. A freshly made standard ferrous solution, well acidified with sulphuric acid, may be used in place of the dry salt.

EXAMPLE: 0·5 gm. pure potassium dichromate was taken for analysis, and to its acid solution 4·15 gm. ferrous ammonium sulphate added. 3·3 c.c. of $^{N}/_{10}$ dichromate were required to oxidize the excess of iron salt; it was found that 0·7 gm. of the salt = 17·85 c.c. dichromate, consequently 3·3 c.c. of the latter were equal to 0·1299 gm. iron salt; this deducted from the quantity originally used left 4·0201 gm., which multiplied by 0·1255 gave 0·504 gm. instead of 0·5 gm.

In the case of lead chromate being determined in this way, it is best to mix both the chromate and the ferrous salt together in a mortar, rubbing them to powder, adding hydrochloric acid, stirring well together, then diluting with water and titrating as before. Where pure ferrous ammonium sulphate is not at hand, a solution of iron wire in sulphuric acid, freshly made, and of ascertained strength, may be used.

2. Determination of Chromates by Distillation with Hydrochloric Acid.

When chromates are boiled with an excess of strong hydrochloric acid in one of the apparatus (fig. 35 or 36), every 1 eq. of chromic acid liberates 3 eq. chlorine. For instance, with potassium dichromate the reaction may be expressed as follows —

$$K_2Cr_2O_7 + 14HCl = 2KCl + Cr_2Cl_6 + 7H_2O + 3Cl_2.$$

If the liberated chlorine is conducted into a solution of potassium iodide, 3 eq. of iodine are set free, and can be determined by $^N/_{10}$ arsenite or thiosulphate. 3 eq. of iodine so obtained (= 380·76) represent 1 eq. chromic acid (= 100). The same decomposition takes place by mere digestion, as described on page 144.

3. Chrome Iron Ore, Steel, etc.

The ore varies in quality, some samples being very rich in chromium, while others are very poor. In all cases the sample is to be first of all brought into *extremely fine powder.* About a gram is rubbed tolerably fine in a steel mortar, then finished fractionally in an agate mortar.

Christomanos recommends that the coarse powder should be ignited for a short time on platinum previous to powdering with the agate mortar, after that it should be sifted through the finest material that can be used, and the coarser particles returned to the mortar for regrinding.

Previous to analysis it should be again ignited, and the analysis made on the dry sample.

O'Neill's Process.—The very finely powdered ore is fused with ten times its weight of potassium bisulphate for twenty minutes, taking care that it does not rise over the edge of the platinum crucible; when the fusion is complete, the molten mass is caused to flow over the sides of the crucible, so as to prevent the formation of a solid lump, and the crucible set aside to cool. The mass is transferred to a porcelain dish, and lixiviated with warm water until entirely dissolved (there must be no black residue, otherwise the ore is not completely decomposed); sodium carbonate is then added to the liquid until it is strongly alkaline; it is then brought on a filter, washed slightly, and the filter dried. When perfectly dry, the precipitate is detached from the filter as much as possible; the filter burned separately; the filter ash and precipitate mixed with about twelve times the weight of the original ore of a mixture of two parts potassium chlorate and three parts sodium carbonate, and fused in a platinum crucible for twenty minutes or so; the resulting mass is then treated with boiling water, filtered, and the filtrate titrated for chromic acid as in (1).

The ferric oxide remaining on the filter is titrated, if required, by any of the methods described under Iron.

Britton's Process.—Reduce the mineral to the finest possible state of division in an agate mortar. Weigh off 0·5 gm., and add to it 4 gm. of flux, previously prepared, composed of one part potassium chlorate and three parts soda-lime; thoroughly mix the mass by triturating in a porcelain mortar, and then ignite in a covered platinum crucible at a bright-red heat for an hour and a half or more. Twenty minutes is sufficient with the gas blowpipe. The mass will not fuse but when cold can be turned out of the crucible by a few gentle taps, leaving the interior of the vessel clean and bright. Triturate in the mortar again and transfer the powder to a tall beaker, add about 20 c.c. of hot water, and boil for two or three minutes; when cold add 15 c.c. of HCl, and stir with a glass rod, till the solid matter, with the exception probably of a little silica in flakes, becomes dissolved. Both the iron and chromium will then be in the highest state of oxidation—Fe_2O_3 and Cr_2O_3. Pour the fluid into a white porcelain dish, and dilute with washings of the beaker to about 100 c.c. Immediately after, add cautiously 1 gm. of metallic iron of known purity, or an equivalent quantity of ferrous ammonium sulphate previously dissolved in dilute sulphuric acid, and further dilute with cold water to about 150 c.c. Titrate with $^N/_{10}$ permanganate the amount of ferrous oxide remaining. The difference between the amount of iron found and of the iron weighed will be the amount oxidized to sesquioxide by the chromic acid. Every one part so oxidized will represent 0·31035 of Cr or 0·45359 of Cr_2O_3, in which last condition the substance usually exists in the ore.

If the amount of iron only in the ore is to be determined, the process is still shorter. After the fluxed mineral has been ignited and reduced to powder as already directed, dissolve it by adding first, 10 c.c. of hot water and applying a gentle heat, and then 15 c.c. of HCl, continuing the heat to incipient boiling till complete decomposition has been effected; cool by immersing the tube in a bath of cold water, add pieces of pure metallic zinc sufficient to bring the iron to the condition of protoxide and the chromium to sesquioxide, and apply heat till small bubbles of hydrogen cease and the zinc has become quite dissolved; then nearly fill the tube with *cold* water, acidulated with one-tenth of sulphuric acid, and pour the contents into the porcelain dish, add *cold* water to make up the volume to about 250 c.c., and titrate with standard permanganate or dichromate.

Sell's Process.—This method[1] is carried out by first fusing the finely ground ore with a mixture of sodium bisulphate and fluoride in the proportion of 1 mol. bisulphate and 2 mol. fluoride, and subsequent titration of the chromic acid by standard thiosulphate and iodine.

From 0·1 to 0·5 gm. of the ore is placed on the top of ten times its weight of the above-mentioned mixture in a large platinum crucible, and ignited for fifteen minutes; an equal weight of sodium bisulphate is then added, and well incorporated by fusion and stirring with a platinum wire; then a further like quantity of bisulphate added in the same way. When complete decomposition has taken place, the mass is boiled with water acidulated with sulphuric acid, and the solution diluted to a definite volume according to the quantity of ore originally taken.

To ensure the oxidation of all the chromium and iron previous to titration, a portion, or the whole, of the solution is heated to boiling, and permanganate added until a permanent red colour is produced. Sodium carbonate is then added in slight excess, and sufficient alcohol to destroy the excess of permanganate; the manganese precipitate is then filtered off, and the clear solution titrated with $^N/_{10}$ thiosulphate and iodine.

---

[1] *J. C. S.*, 1879, p. 292.

The author states that the analysis of an ore by this method may be accomplished in one hour and a half.

For the oxidation of salts of chromium, the same authority recommends boiling with potash or sodium carbonate (to which a small quantity of hydrogen peroxide is added) for fifteen minutes.

For the preliminary fusion and oxidation of chrome iron ore, Dittmar recommends a mixture of two parts borax glass and one and a half part each of sodium and potassium carbonates. These are fused together in a platinum crucible until all effervescence ceases, then poured into a large platinum basin or upon a clean iron plate to cool, broken up, and preserved for use.

Ten parts of this mixture are used for one part of chrome ore, and the fusion made in a platinum crucible, closed for the first five minutes, then open for about forty minutes, frequently stirring with a platinum wire, and using a powerful Bunsen flame. The gas blowpipe hastens this method considerably.

The above described methods of treating the ores of chromium so as to obtain complete decomposition are apparently now superseded to a great extent by the use of sodium peroxide, but the action of this reagent upon platinum, gold, silver, nickel, or porcelain is so energetic that its use requires great care. Many well-known authorities on the analysis of chrome ores use a basic mixture such as was first suggested by Clark, but modified by Stead, i.e. magnesia or lime four parts, potassium and sodium carbonates of each one part. Clark's original mixture of magnesia and caustic soda acts on platinum, but Stead's mixture does not.

The fusion is made by mixing the very finely ground sample with ten times its weight of the basic mixture in a platinum crucible, and heating to bright redness at the back of a gas muffle for about an hour. When the crucible is removed and cool the mass is found sintered together. It is removed to a beaker, and the crucible washed out with water and dilute sulphuric acid. The decomposition is generally complete, but if any black specks are found they must be separated by filtration, dried, and again fused with some of the basic mixture; finally the whole is mixed with excess of ferrous salt, and the unoxidized iron titrated with dichromate as before described.

Rideal and Rosenblum[1] give a series of experiments on the determination of chromium in ores, steels, etc., and on the use of sodium peroxide, which latter they find has a most destructive effect on all kinds of vessels in which the decomposition is made. Nickel seems the best material if not exposed to too high a temperature, but they found also that a good deal of nickel was dissolved from the crucibles by the sulphuric acid used to dissolve the melt, and they therefore attach great importance to the filtration of the aqueous solution of the melt, so as to remove nickel and iron oxides, which otherwise interfere with the titration by masking the colour of the indicator.

---

[1] *J. S. C. I.*, 1895, **14**, 1017.

Rideal and Rosenblum's experiments appear to show that sodium peroxide, if certain conditions be observed in its use, is a very valuable reagent for the analysis of chrome ore, ferrochrome, and chrome steel, as it removes the two main defects of former methods, viz., the necessity of repeated fusion to effect complete decomposition and the inconvenient slowness of these processes. The conditions which should be observed are summarized by them as follows:—

(1) Great care should be taken to reduce the chrome ore or the ferrochrome to an almost impalpable powder. This can be done without much difficulty if the ore or the alloy be crushed in a steel mortar until a powder is obtained which will pass through a linen bag. This powder is then ground in an agate mortar to the required degree of fineness, a little water being added to facilitate the grinding.

(2) The water solution of the melt, before acidulation, must be freed from an excess of sodium peroxide. Whenever sodium ferrate or sodium manganate is formed during the fusion it must be decomposed in the water solution of the melt.

(3) As the result of the analysis depends to a large extent upon the titration, and especially upon a clear perception of its final point, it is important that the solution in which the chrome is to be determined should be as free as possible from other metallic salts, as for instance, iron, manganese, and nickel salts. We have also observed that the ferricyanide solution which is used as an indicator is most satisfactory when it contains no more than 1 per cent. of ferricyanide.

Ferrochrome, Chromium Steel, etc.—Spüller and Brenner[1] describe an improved method which gives better results than the previous method advocated by Spuller and Kalman.

Method of Procedure for Ferrochrome: 0·35 gm. of the finely powdered sample, mixed in a silver dish with 2 gm. of dry powdered sodium hydroxide and covered with 4 gm. of sodium peroxide, is heated until the mixture begins to melt, when, as a consequence of the strong chemical action, the whole mass soon becomes liquefied. The dish is then again heated for ten minutes over a powerful burner, and 5 gm. of sodium peroxide are cautiously added, stirring all the while with a silver spatula. After heating for thirty minutes more, another 5 gm. of sodium peroxide are added and the heating continued for twenty minutes, when a final 5 gm. of the peroxide are added.

When cold, the silver basin is placed in a deep porcelain dish and filled with water; when the lixiviation is completed, which takes a few minutes only, the silver dish is lifted out and well rinsed with hot water. A brisk current of CO_2 is then passed through the liquid for half an hour, the whole allowed to cool, transferred to a litre measure, and made up to the mark with water. After shaking and filtering, 250 c.c. are taken and the chromic acid titrated by a permanganate solution of which 1 c.c. equals about 0·005 gm. of iron, and a solution of ferrous ammonium sulphate containing 7 gm. of the salt in 500 c.c. The chromium solution is diluted with 1 litre of cold water which has been previously boiled and acidified with 20 c.c. of sulphuric acid (1 : 5 by volume); 100 c.c. of ferrous ammonium sulphate are added, and the mixture titrated back with permanganate. The strength of the ferrous solution is determined by a blank experiment under similar conditions. If the solution of the melt appears green, it is advisable to add first a few c.c. of permanganate and then some more sodium peroxide, when a pure yellow liquid will be obtained.

---

[1] *Chem. Zeit.*, 1897, **21**, 3, 4.

METHOD OF PROCEDURE FOR CHROME STEEL: 2 gm. of the sample are dissolved in 20 c.c. of warm hydrochloric acid contained in a porcelain dish, 10 c.c. of dilute sulphuric acid (1 : 1) are added, and the whole evaporated to dryness; the residue is then transferred to a silver dish and heated with 2 gm. of sodium hydroxide and 5 gm. of sodium peroxide, until the sulphates are decomposed and the mass begins to cake. A strong heat is now applied and another 5 gm. of the peroxide added. When the mass begins to fuse, it is well stirred with a silver spatula, and after twenty minutes another 5 gm. of peroxide are added; after another twenty minutes, when the oxidation is complete, a further addition of 5 gm. of the soda is made and the mass is allowed to cool. The melt is then extracted as in the former case, but the liquid is made up to 500 c.c. only, and 250 c.c. of the filter (= 1 gm. of sample) are taken for the titration of the chromium. In this case, the authors prefer titrating according to Zulkowsky's method, i.e. the liquid is put into a tall, narrow beaker, mixed with 10 c.c. of a 10 per cent. solution of potassium iodide, and acidified with pure hydrochloric acid. To another beaker containing 20 c.c. of a solution of potassium dichromate (0·990 gm. per litre, 1 c.c. = 0·00035 gm. Cr.), 250 c.c. of water are added, then 10 c.c. of a 10 per cent solution of potassium iodide and a little hydrochloric acid. After being left for fifteen minutes in a dark place, both liquids are titrated with solution of sodium thiosulphate containing 4·96 gm. of the salt per litre. The amount of chromium being known in the one solution, the quantity contained in the other is readily calculated.

Rideal and Rosenblum have obtained excellent results with ferrochrome by fusion with sodium peroxide alone. The manner of procedure was as follows:—

About 0·5 gm. of a very finely powdered ferrochrome was mixed with 3 gm. of sodium peroxide and heated very gently in a nickel crucible, until the mass began to melt, and then to glow by itself. The heating was then continued for ten minutes, and after the mass was partially cooled 1 gm. of sodium peroxide was added and the heating continued for another five minutes.

The crucible, when still moderately warm, was placed in a suitable porcelain basin, which was then half filled with hot water and covered with a clock glass. The melt easily dissolved in hot water, the solution obtained being of a deep purple colour, due to sodium ferrate, which is abundantly formed during the fusion. The solution also contained sodium manganate, resulting from the oxidation of the manganese which is present in ferrochrome.

To decompose both these salts a small quantity of sodium peroxide was added, on which the solution immediately lost its purple colour. The solution was then boiled for ten minutes to decompose the excess of sodium peroxide, and the insoluble residue of iron, nickel, and manganese oxide was filtered off. An excess of sulphuric acid was then added to the solution, and after cooling it was titrated in the usual manner with permanganate.

Rapid Methods for the Determination of Chromium in Iron and Steel.—Galbraith's method, modified somewhat by Stead.[1]

The sample (2 gm.) is dissolved in 30 c.c. dilute sulphuric acid (1 to 3), filtered, the solution diluted to about 300 c.c and heated to boiling. Strong solution of potassium permanganate is now added until the red colour is permanent for ten minutes, then 80 c.c. of 10 per cent. hydrochloric acid, and the liquid heated until decolorized; 150 c.c. of water are added, about 100 c.c. boiled off to expel the chlorine, and the chromium is then titrated with ferrous sulphate and dichromate as on p. 133. The residue insoluble in dilute sulphuric acid is mixed with 0·5 gm. of the basic mixture previously mentioned, and heated to intense redness for half an hour; the chromium is afterwards titrated in hydrochloric acid solution with ferrous sulphate and dichromate.

Another process consists in dissolving 2 gm. of the sample in hydrochloric acid; without filtering, the liquid is nearly neutralized with a 2 per cent. solution of caustic soda, and, after diluting to 300 c.c., 10 c.c. of a 5 per cent. solution of sodium phosphate and 30 gm. of sodium thiosulphate are added. After boiling to expel the SO_2, 20 c.c. of a saturated solution of sodium acetate are added, and the boiling continued for five minutes; the precipitated chromium phosphate is then washed with a 2 per cent. solution of ammonium nitrate, dried, calcined, and fused with the basic mixture. The melt, dissolved in 30 c.c. of hydrochloric acid and 150 c.c. of water, is boiled for ten minutes and titrated. The process may be used in presence of vanadium. In this case, the chromium must be titrated by means of ferrous sulphate and permanganate in presence of sulphuric acid.

Gregory and McCallum's Method.[2]—By this method a determination can be made in less than an hour. 0·2 gm. of the sample is dissolved in as little nitric acid (1·2 sp. gr.) as possible, the solution diluted to 50 c.c., 1 gm. of silver nitrate and 10 gm. of ammonium persulphate added, and the liquid boiled for 5 minutes. 0·25 gm. of ammonium chloride is added, i.e. sufficient to precipitate nearly all the silver as chloride (the presence of silver nitrate ensures the absence of free chlorine), and the solution is again boiled, when any permanganic acid is decomposed, the manganese being partly precipitated as the hydrated peroxide, and partly converted into manganous chloride. After cooling and making up to a definite volume, an aliquot portion of the solution is titrated with ferrous sulphate and standard dichromate solution in the usual manner. If the sample be free from manganese, the addition of ammonium chloride is omitted, but after the first boiling a few c.c. of a dilute solution of manganese sulphate are added. If any persulphate remain undecomposed a pink colour will be produced, which is just destroyed by the addition of hydrogen peroxide drop by drop. The solution is again boiled, cooled, and titrated as above.

---

[1] *Jour. Iron and Steel Institute*, 1893, 153.

[2] *J. C. S.*, 1907, **91**, 1846.

Evans's Colorimetric Method,[1] for Small Amounts of Chromium in Steel (under 0·05 per cent.), for the determination of which the foregoing methods cannot be relied upon. 4 gm. of the sample are dissolved by heating with 30 c.c. sulphuric acid (1 : 3) and 20 c.c. of water, 5 to 10 c.c. of nitric acid are added, and the solution boiled to expel nitrous fumes. About 25 gm. of ammonium phosphate are then added, and 250 c.c. of water (and more nitric acid if ferric phosphate separates), and the whole again heated to boiling. To the boiling liquid a saturated solution of potassium permanganate is added two or three drops at a time till there is an excess, as shown by a permanent precipitate of manganese dioxide or by a permanent red colour, then a further excess of about 12 drops, and the boiling continued for 15 minutes. The whole of the liquid is at once poured, slowly and with constant shaking, into 120 c.c. of 20 per cent. sodium hydroxide solution, which has previously been heated to boiling for some minutes with excess of permanganate, and then treated with 10 c.c. of 5 per cent. manganese sulphate solution. The resulting mixture, if acid, is rendered strongly alkaline with sodium hydroxide, cooled, acidified strongly with acetic acid, diluted to 500 c.c., allowed to settle for a short time, then filtered through a dry filter, the first few c.c. being rejected. 100 c.c. of the filtrate are placed in one Nessler glass, and rather less than that volume of distilled water in another, 20 c.c. of sulphuric acid (1 : 3) added to each, and $^{N}/_{100}$ dichromate solution run into the blank until the colours match, when the blank is made up to 100 c.c. If nickel or cobalt be present, 100 c.c. of the filtrate are heated to boiling, and sodium hydroxide solution added until a precipitate separates. The liquid is cooled, filtered through a small filter into a Nessler glass, acidified with sulphuric acid, and the colorimetric determination made as above.

$$\text{c.c. of } ^{N}/_{100}\ K_2Cr_2O_7 \text{ used} \times {\cdot}0217 = \text{Cr per cent.}$$

Iodimetric Determination of Chromic Acid.—H. P. Seubert and Henke[2] have devised a method which depends upon the reaction:

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 = 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2.$$

Under ordinary circumstances the action takes considerable time. The authors have made an exhaustive investigation of its rate of progress when the different bodies are present in different quantities. Increasing the proportion of acid accelerates the reaction more than increasing the proportion of potassium iodide does; dilution greatly retards it. The following are convenient proportions to use: Dichromate, 0·05 gm.; potassium iodide, 0·5 gm.; sulphuric acid, 1·8 gm.; total volume, 100 c.c. If less than 0·05 gm. of dichromate be present, the other quantities should still be kept the same. If there be more dichromate, the iodide and acid should be proportionately increased without adding more water, unless there be more than 0·25 gm. The reaction is complete in about six minutes. The liquid should then be diluted and titrated with thiosulphate solution, using starch as indicator.

---

[1] *Analyst*, 1921, **46**, 38.

[2] *Zeit. f. angew. C.*, 1900, **14**, 1117.

COBALT.

Co = 58·97.

Determination by Permanganate and Mercuric Oxide (C. Winkler).

THE volumetric determination of cobalt, especially in the presence of other metals, is not yet very satisfactory. The method here mentioned is worthy of notice, and with an alteration suggested by H. B. Harris[1] is capable of giving fair technical results. This alteration consists in carrying out the titration in a hot solution instead of a cold one, as appears to have been done by Winkler. If an aqueous solution of cobaltous chloride or sulphate be treated with an emulsion of precipitated mercuric oxide, no decomposition ensues; but on the addition of permanganate to the mixture, hydrated cobaltic and manganic oxides are precipitated, and the mercuric oxide is simply used to separate mechanically the resulting oxides. It is probable that no definite equation can be given for the reaction, and therefore practically the working effect of the permanganate is best determined by a standard solution of cobalt of known strength, say metallic cobalt dissolved as chloride, or neutral cobaltous sulphate.

METHOD OF PROCEDURE: The solution of about 0·1 to 0·2 gm. of the metal, free from any great excess of acid is placed in a flask, diluted to about 200 c.c., and a tolerable quantity of mercuric emulsion (precipitated from the nitrate or perchlorate by alkali and washed) added. Permanganate from a burette is then slowly added to the hot solution with constant shaking until the rose colour appears in the clear liquid above the bulky brownish precipitate.

The appearance of the mixture is somewhat puzzling at the beginning, but as more permanganate is added the precipitate settles more freely, and the end as it approaches is very easily distinguished. The process is complete when the rose colour is persistent for a minute or two; subsequent bleaching must not be regarded.

The actual decomposition as between cobaltous chloride and permanganate may be formulated thus—

$$6CoCl_2 + 5HgO + K_2Mn_2O_8 + H_2O = 3Co_2(OH)_6 + 5HgCl_2$$
$$+ 2KCl + 2MnO_2H_2O$$

but as this exact decomposition cannot be depended upon to take place in all mixtures, it is not possible to accept systematic numbers calculated from normal solutions.

Solutions containing manganese, phosphorus, arsenic, active chlorine, oxygen compounds, or organic matter, cannot be used in this method of determination; moderate quantities of copper or lead are of no consequence. Nor is antimony when its quantity is double or more that of the cobalt, but if less the results are too high.

A further modification of this method was advocated by von Reis and Wiggert, and possesses the advantage of being easy and simple in execution. Very fair results were obtained by H. B. Harris on trial at the same time as the examination of Winkler's method.

---

[1] *J. A. C. S.*, 1898, **20**, 173.

Method of Procedure: The solution of cobalt is mixed with an emulsion of zinc oxide and heated to boiling. A standard solution of permanganate is then added in known quantity, but more than enough to precipitate the oxidized cobalt. The latter precipitate settles to the bottom, the excess of permanganate is then found by titration with a standard solution of ferrous ammonium sulphate.

R. L. Taylor[1] has experimented on Rose's method of separating cobalt from nickel, and has improved it by using a perfectly neutral solution instead of a strongly acid one as used by Rose; the latter neutralized the solution by calcium or barium carbonate, but the CO_2 so produced retarded or altogether stopped the precipitation of the cobalt oxide. By the new process the result is that a dilute neutral solution of cobalt may be quantitatively precipitated by barium or calcium carbonate in presence of bromine water. If the liquid from which the cobalt is to be precipitated is acid, the acid must be neutralized by an excess of carbonate and well boiled to expel all the CO_2, and then cooled before the bromine water is added. Not only CO_2 but zinc also stops the precipitation.

The composition of the black oxide is not quite clear, but it is fairly constant in composition, and if dissolved with HCl and KI the amount is ascertained by titrating the liberated iodine. The method has been tested by J. H. Davidson in the assay of cobalt ores, and he finds it much more rapid than the usual methods and sufficiently accurate for assay purposes.

For other methods for the determination of Cobalt, see under Nickel.

COPPER.

Cu = 63·57.
1 c.c. N/10 solution = 0·006357 gm. Cu.
Iron × 1·138 = Cu.
Ferrous Ammonium sulphate × 0·1622 = Cu.

1. Reduction by Grape Sugar and Subsequent Titration with Ferric Chloride and Permanganate (Schwarz).

This process is based upon the fact that grape sugar precipitates cuprous oxide from an alkaline solution of the metal containing tartaric acid; the oxide so obtained is collected and mixed with ferric chloride and hydrochloric acid. The result is the following decomposition:—

$$Cu_2O + Fe_2Cl_6 + 2HCl = 2CuCl_2 + 2FeCl_2 + H_2O.$$

Each equivalent of copper reduces one equivalent of ferric to ferrous chloride, which is determined by permanganate with due precaution. The iron so obtained is calculated into copper by the requisite factor.

Method of Procedure: The weighed substance is brought into solution by nitric or sulphuric acid or water, in a porcelain dish or glass flask, and most of the acid in excess neutralized with sodium carbonate; neutral potassium tartrate is then added in not too large quantity, and the precipitate so produced dissolved to a clear blue liquid by adding caustic potash or soda in excess; the vessel is next heated cautiously to about 50° C. in the water bath, and sufficient grape sugar added to precipitate the copper present; the heating is continued until the precipitate is of a bright red colour, and the upper liquid is brownish at the edges from the action of the alkali on the sugar; the temperature must never exceed 90° C. When the mixture has somewhat cleared, the upper fluid is poured through a moistened filter, and afterwards the precipitate brought on the same, and washed with hot water till thoroughly clean; the precipitate which may adhere to the dish or flask is well washed, and the filter containing the bulk of the protoxide put with it, and an excess of solution of ferric chloride (free from nitric acid or free chlorine) added, together with a little sulphuric acid; the whole is then warmed and stirred until the cuprous chloride is all dissolved. It is then filtered into a good-sized flask, the old and new filters being well washed with hot water, to which at first a little free sulphuric acid should be added, in order to be certain of dissolving all the oxide in the folds of the paper. The entire solution is then titrated with permanganate in the usual way. Dichromate may also be used, but the end of the reaction is not so distinct as usual, owing to the turbidity produced by the presence of copper.

---

[1] *C. N.*, 1903, **88**, 184.

A modification of this permanganate method, which gives very good technical results, has been devised by R. K. Meade,[1] in which the copper is precipitated as thiocyanate. The author considers it superior in accuracy to the iodide method; but with this I cannot agree, except in certain cases.

METHOD OF PROCEDURE: The copper is brought into solution as a sulphate, either by dissolving it in sulphuric acid or by evaporation of its solution with sulphuric acid. The greater part of the free acid is neutralized by ammonia, the solution warmed, sulphurous acid added until the solution smells strongly of the reagent, and then a slight excess of ammonium or potassium thiocyanate. The copper is immediately precipitated as cuprous thiocyanate. Stirring and warming renders the precipitate heavy and easily handled. The solution is filtered through asbestos, using the pump, and well washed. The precipitate and filter are thrown into the beaker in which the precipitation was made and heated with a solution of caustic soda or caustic potash. Double decomposition takes place. Hydrated cuprous oxide and potassium or sodium thiocyanate result—

$$2CuSCN + 2KOH = Cu_2(OH)_2 + 2KSCN.$$

The oxide is filtered on asbestos and washed well with hot water. The precipitate and filter are again placed in the same beaker and an excess of ferric chloride or ferric sulphate (free from nitric acid, free chlorine, or ferrous salts), together with a little dilute sulphuric acid, added. The copper oxide reduces a corresponding amount of iron from the ferric to the ferrous condition—

$$Cu_2O + Fe_2Cl_6 + 2HCl = 2CuCl_2 + 2FeCl_2 + H_2O.$$

The beaker is warmed and stirred until all the copper oxide is dissolved. The solution is then poured through a perforated platinum disc, and the asbestos which remains behind upon it washed with water, to which has been added a little sulphuric acid and a little ferric chloride or sulphate. The solution is then titrated with permanganate. The iron equivalent to the permanganate used multiplied by 1·138 gives the weight of copper in the sample.

---

[1] *J. A. C. S.*, 1898, **20**, 610.

Instead of sulphurous acid, ammonium or sodium bisulphite may be used to reduce the copper. A solution of equal weights of sodium bisulphite and potassium thiocyanate answers well as a reagent for the precipitation of the metal. Since copper is the only metal precipitated by an alkali thiocyanate from an acid solution, the presence of arsenic, antimony, bismuth, zinc, and other elements which render the electrolytic, the cyanide, and the iodine methods inaccurate, will not affect the results.

The caustic alkali solution, used to convert the cuprous thiocyanate into cuprous hydroxide, must not be too strong, or some of the metal will go into solution, colouring the liquid blue. About a half normal solution of caustic potash, made by dissolving 28 gm. of the salt in a litre of water, is a convenient strength. Either ferric sulphate or ferric chloride may be used to dissolve the cuprous oxide. The former is probably the safer, but the latter appears to dissolve the precipitate the more readily of the two.

2. Reduction by Zinc and Subsequent Titration with Ferric Chloride and Permanganate (Fleitmann).

The metallic solution, free from nitric acid, bismuth, and lead is precipitated with clean sticks of pure zinc; the copper collected, washed, and dissolved in a mixture of ferric chloride and hydrochloric acid; a little sodium carbonate may be added to expel the atmospheric air. The reaction is—

$$Cu + Fe_2Cl_6 = CuCl_2 + 2FeCl_2.$$

When the copper is all dissolved, the solution is diluted, and titrated with permanganate; 55·85 Fe = 31·79 Cu, or 1 Fe = ·5692 Cu.

If the original solution contains nitric acid, bismuth, or lead, the decomposition by zinc must take place in an ammoniacal solution, from which the precipitates of either of the above metals have been removed by filtration; the zinc must in this case be finely divided and the mixture warmed. The copper is all precipitated when the colour of the solution has disappeared. It is washed first with hot water, then with weak HCl and water to remove the zinc, again with water, and then dissolved in the acid and ferric chloride as before.

3. Iodimetric Determination after Precipitation as Cuprous Iodide.

This excellent method is based on the fact that when potassium iodide is mixed with a salt of copper in acid solution cuprous iodide is precipitated as a dirty white powder and iodine set free. If the latter is then immediately titrated with thiosulphate and starch, the corresponding quantity of copper is found.

$$2CuSO_4 + 4KI = Cu_2I_2 + 2K_2SO_4 + I_2.$$

The solution of the metal, if it contain nitric acid, is evaporated with sulphuric acid till the former is expelled, or the nitric acid is neutralized with sodium carbonate, and acetic acid added; the sulphate solution must be neutral, or only faintly acid; excess of acetic acid is of no consequence, and therefore it is always necessary to get rid of all free mineral acids and work only with free acetic acid.

J. W. Westmoreland,[1] who has had very large experience in examining a variety of copper products, and has worked the process in my own laboratory, strongly recommends it for the determination of copper in its various ores, etc. The metal may very conveniently be separated from a hot sulphuric acid solution by sodium thiosulphate: this gives a flocculent precipitate of subsulphide mixed with sulphur, which filters readily, and can be washed with hot water. Arsenic and antimony, if present, are also precipitated; tin, zinc, iron, nickel, cobalt, and manganese are not precipitated. On igniting the precipitate most of the arsenic and the excess of sulphur are expelled, an impure oxide of copper being left. Sulphuretted hydrogen may of course be used instead of the thiosulphate, but its use is objectionable to many operators; moreover, in some circumstances, a small amount of copper remains in the solution, and iron in small quantity is also precipitated with the copper and cannot be entirely removed by washing. If H_2S is used it should be passed for some time, and the precipitate allowed to stand a few hours to settle; after filtration and washing the CuS should be redissolved in HNO_3 and reprecipitated with the gas, it is then quite free from iron.

Standardizing the Thiosulphate Solution.—Pure electrolytic copper foil is used, a known weight being first dissolved in nitric acid, boiled to expel nitrous fumes, diluted, neutralized with sodium carbonate till a precipitate appears, then acetic acid added till clear. The liquid is then made up to a definite volume, and a quantity equal to about 0·5 gm. Cu taken in a flask or beaker, about ten times the copper weight of potassium iodide added, and when dissolved the thiosulphate is run in from a burette until the free iodine is nearly removed, some starch then added, and the titration finished in the usual way. The thiosulphate will, of course, need to be checked occasionally. See note on p. 206. (Addition of sodium fluoride).

If strictly N/10 thiosulphate is used, each c.c. = 0·006357 gm. Cu.

For technical purposes a useful standard sodium thiosulphate solution is one containing 40 gm. of the crystals in a litre :—

1 c.c. = (approximately) 0·01 gm. Cu.

METHOD OF PROCEDURE: For determining the copper in iron pyrites or burnt ore 5 gm. of the substance should be taken, 2 gm. for 30 to 40 per cent. mattes or 1 gm. for 60 per cent. mattes, and with precipitates it is best to dissolve say 5 gm. and dilute to a definite volume, and take as much as would represent from 0·5 to 0·7 gm. of Cu for titration. The solution is made with nitric acid, to which hydrochloric is also added later on, and then evaporated to dryness with excess of sulphuric acid to convert the bases into sulphates; the residue is treated with warm water and any insoluble $PbSO_4$, etc., filtered off. The filtrate is heated to boiling and precipitated with thiosulphate, this precipitate is filtered off, washed with hot water, dried, and roasted; the resulting copper oxide is then dissolved in nitric acid, and after the excess of acid has been mainly removed by evaporation, sodium carbonate is added so as to precipitate part of the copper and ensure freedom from mineral acid, acetic acid is added till a clear solution is obtained; about 10 parts of potassium iodide to one of copper supposed to be present are then added, and the titration carried out in the usual way.

---

[1] *J. S. C. I.*, 1886, 5, 51.

An excellent modification of this method, much used in America, is described by A. H. Low.[1] A solution of thiosulphate is used containing about 19 gm. per litre, which is standardized upon about 0·2 gm. of pure copper foil dissolved in 5 or 6 c.c. of nitric acid sp. gr. 1·2 in a 250 c.c. flask in the following manner:—

Heat the nitric acid solution to boiling, add 5 c.c. strong bromine water, and again boil till all nitrous fumes and bromine are expelled. As soon as the incrusted matter has dissolved, add a slight excess of ammonia, boil off the excess, then add 3 to 4 c.c. of acetic acid, which dissolves any precipated copper hydroxide (boiling again may be necessary), after cooling and diluting to about 50 c.c. add 3 gm. of KI and titrate with thiosulphate as usual.

METHOD OF PROCEDURE FOR ORES: Treat 0·25 to 0·5 gm. of finely ground ore with 5 or 6 c.c. of nitric acid 1·42 sp. gr., and evaporate nearly to dryness. Dissolve all incrusted matter by heating with 5 c.c. strong hydrochloric acid, add 7 c.c. sulphuric acid and heat, to expel volatile acids, till the sulphuric acid fumes freely. After cooling and diluting with 25 c.c. of water, heat to dissolve any anhydrous ferric sulphate, and filter. The filtrate and washings, which should not much exceed 75 c.c., are received in a small beaker. The copper is now precipitated by means of aluminium as follows:—Place in the beaker two pieces of stout sheet aluminium, about one-sixteenth of an inch in thickness, which, for the sake of convenience in subsequent washing, should be 1½ inch square with the four corners bent, for about a quarter of an inch, alternately up and down at right angles. This prevents the pieces from lying flat against each other or upon the bottom of the beaker. The same pieces may be used repeatedly, as they are but little attacked each time. Cover the beaker and boil gently for 7 to 10 minutes. Unless the bulk of the solution is excessive, this will be quite sufficient for all percentages of copper. Ordinarily the aluminium will be found to be clean, and nearly or quite free from precipitated copper. If, by chance, the copper adheres to any considerable extent, it will usually become loosened by a little additional boiling, or it may be removed by the aid of a glass rod. Rinse the cover and sides of the beaker with cold water. To prevent oxidation of finely divided copper during subsequent washing and at the same time to remove any traces of copper still in solution, add about 15 c.c. strong H_2S water. Transfer the solution back to the original flask, and by means of a jet of H_2S water from a wash-bottle rinse in also as much of the copper as possible, leaving the aluminium behind. Drain the beaker as completely as possible, and temporarily set aside with the aluminium, which may still retain a little copper. Allow the copper in the flask to settle, and then decant the liquid through a filter. Again wash the copper similarly two or three times with about 20 c.c. H_2S water each time, retaining it as completely as possible in the flask. Finally, wash the filter once or twice and endeavour to rinse all metallic particles down into the apex. Now pour upon the aluminium in the beaker 5 c.c. of nitric acid[1] 1·2 sp. gr., and warm the beaker gently, but do not heat to boiling, as the aluminium would be thereby unnecessarily attacked. See that any copper present is dissolved, and pour the hot solution very slowly through the filter, thus dissolving any contained particles of copper, and receive the filtrate in the flask containing the main portion of the copper. Before washing the filter pour upon it 5 c.c. of bromine water, and wash the filter and beaker with hot water. The bromine must be in sufficient excess to give a slight tinge to the filtrate. Boil the filtrate to remove bromine, add excess of ammonia, and proceed as described above for copper foil in standardizing. If the percentage of Cu in the ore does not exceed 20 per cent., the precipitated metal may be washed with H_2S water upon the filter, instead of by decantation, care being taken that the filter is kept filled till the washing is complete, to avoid oxidation.

---

[1] *J. A. C. S.*, 1896, **18**, 458, and 1902, **24**, 1082.

A. M. Fairlie[2] uses ammonium thiocyanate, in preference to sodium thiosulphate or aluminium, to separate the copper.

The cuprous thiocyanate is dissolved in strong nitric acid, the solution boiled till red fumes are no longer evolved, then neutralized with ammonia, acidified with acetic acid, KI added and the titration carried out in the usual way. The presence of much ammonium acetate must be avoided.

Copper may also be separated as cuprous oxide by means of glucose, and this oxide dissolved in nitric acid, and the determination proceeded with as usual.

Note.—Should any *iron* be present in the copper solution to be titrated with thiosulphate its effect may be eliminated by the addition of sodium fluoride solution, as recommended by Fraser.[3] The solution used is made by diluting a saturated aqueous solution of sodium fluoride with an equal volume of water and filtering, 50 c.c. of this being added to the copper solution immediately before the potassium iodide is added. A similar addition of fluoride should be made when standardizing thiosulphate against electrolytic copper.

4. Determination by Potassium Cyanide (Parkes and C. Mohr).

(A solution containing 40 gm. potassium cyanide per litre is used)
1 c.c. = (about) ·01 gm. copper.

This well-known and much used process for determining copper depends upon the decolorization of an ammoniacal solution of copper by potassium cyanide. The reaction (which is not absolutely uniform with variable quantities of ammonia) is such that a double cyanide of copper and ammonia is formed; cyanogen is also liberated, which reacts on the free ammonia, producing urea, oxalate of urea, ammonic cyanide and formate (Liebig). Owing to the influence exercised by variable quantities of ammonia, or its neutral salts, upon the decolorization of a copper solution by the cyanide, it has been suggested by Beringer to substitute some other alkali for ammonia in neutralizing the free acid in the copper solution. The suggestion has been adopted by Davies[1] and by Fessenden[2] who both recommend sodium carbonate. My own experiments completely confirm their statement that none of the irregularities observed with variable quantities of ammonia or its salts occur with soda or potash. Suppose, for example, that copper has been separated as sulphide, and brought into solution by nitric acid, the free acid is neutralized with Na_2CO_3, and an excess of it added to redissolve the precipitate. The cyanide solution is then cautiously run into the light blue solution until the colour is just discharged. My own experience is that it is impossible to redissolve the whole of the precipitate without using a very large excess of soda; but there is no need to add such an excess, as the precipitate easily dissolves when the cyanide is added. I have used a modification of this method which gives excellent results, viz., to neutralize the acid copper solution either with Na_2CO_3 or NaHO, add a trifling excess, and then 1 c.c. of ammonia 0·960 sp. gr.; a deep blue clear solution is at once given, which permits of very sharp end-reaction with the cyanide.

---

[1] Videgren (*Z a. C.*, 1909, 539) prefers to dissolve in a mixture of potassium chlorate and hydrochloric and sulphuric acids. If arsenic or antimony is present, sodium acetate is added before titrating. The end-points obtained are said to be much sharper than with Low's method of solution.

[2] *Eng. and Mining J.*, 1904, 787.

[3] *J. S. C. I.*, 1915, **34**, 462, also 1918, **37**, 92 T.

J. J. and C. Beringer adopted the method of neutralizing the acid copper solution with soda, then adding ammonia, but the proportion they recommend is larger than necessary.

In standardizing the cyanide, it is advisable so to arrange matters that copper is precipitated with soda exactly as in the titration of a copper ore; that is to say, free nitric or nitro-sulphuric acid should be added, then neutralized with slight excess of soda, cleared with 1 c.c. of ammonia, then titrated with cyanide. Large quantities of nitrate or sulphate of soda or potash, however, make very little difference in the quantity of cyanide used.

METHOD OF PROCEDURE: Dissolve 0·2 gm. of pure electrolytic copper foil in 5 c.c. of pure nitric acid in a 150 c.c. beaker, add about 50 c.c. of water, make the solution just alkaline by addition of sodium carbonate or hydrate solution, add 1 c.c. of 0·96 ammonia, and run the cyanide from a burette into the liquid, with constant stirring, till it is just decolorized.

It has generally been thought that where copper and iron occur together, it is necessary to separate the latter before using the cyanide. F. Field,[3] however, has stated that this is not necessary; and I can fully endorse his statement that the presence of the suspended ferric oxide is no hindrance to the determination of the copper; in fact, it is rather an advantage, as it acts as an indicator to the end of the process.

While the copper is in excess, the oxide possesses a purplish-brown colour, but as this excess lessens, the colour becomes gradually lighter, until it is orange-brown. If it be now allowed to settle, which it does very rapidly, the clear liquid above will be found nearly colourless. A little practice is of course necessary to enable the operator to hit the exact point.

---

[1] *C. N.*, 1888, **58**, 131.

[2] *C. N.*, 1890, **61**, 183, 253. See also Fernekes and Koch, *J. A. C. S.*, 1905, **27**, 1224.

[3] *C. N.*, 1860, **1**, 25.

It is impossible to separate the ferric oxide by filtration without leaving some copper in it, and no amount of washing will remove it. For example, 10 c.c. of a copper solution with 10 c.c. of ferric solution were directly titrated with cyanide after treatment with NaHO in slight excess and 1 c.c. of ammonia. The cyanide required was 12 c.c. Another 10 c.c. of the same copper and iron solutions were then precipitated with soda and ammonia in same proportions. This gave a complete solution of the copper with the ferric oxide suspended in it. The solution was filtered and the ferric oxide well washed with hot water, then the filtrate cooled and titrated with cyanide, 9·5 c.c. only being required. On treating the ferric oxide on the filter with nitric acid, neutralizing with NaHO and NH_3 in proper proportions exactly, 2·5 c.c. of cyanide were required, showing that the ferric oxide had retained 20 per cent. of the copper.

I strongly recommend that operators who have to deal with copper determination in samples containing much iron should practise the use of the cyanide method in the presence of the iron, and accustom their eyes to the exact colour which the ferric oxide takes when the titration is finished, always, however, with this proviso, that the cyanide solution is standardized upon a known weight of copper in the presence of a moderate amount of iron.

The solution of potassium cyanide should be titrated afresh at intervals of a few days. A solution containing 20 gm. pure potassium cyanide per litre is convenient. Further details of this process are given on p. 212 (8).

Dulin[1] advocates the cyanide process for copper ores as follows:—

METHOD OF PROCEDURE The ore is treated in the way described on p. 204 to obtain a solution of the copper practically free from silver and lead. The copper is then precipitated upon aluminium foil as there mentioned. Should cadmium be present it is also precipitated to some extent, but only after the copper is thrown down. If care be taken to stop the boiling immediately after the copper is precipitated, which a practised eye will readily detect, the amount of cadmium precipitated is so small as to cause no sensible error. The liquid being decanted from the copper and foil, the latter are washed well with hot water, taking care to lose no metal; when quite clean, dilute nitric acid is added and boiled till the copper is dissolved, the liquid then neutralized with excess of ammonia, and titrated with cyanide in the usual way.

5. Determination as Sulphide (Pelouze).

It is first necessary to have a solution of pure copper of known strength, which is best made by dissolving 39·286 gm. of pure re-crystallized cupric sulphate in 1 litre of water; each c.c. will contain 0·01 gm. Cu.

Precipitation in Alkaline Solution.—This process is based on the fact that if an ammoniacal solution of copper is heated to from 40° to 80° C., and a solution of sodium sulphide added, the whole of the copper is precipitated as oxysulphide, leaving the liquid colourless. The loss of colour indicates, therefore, the end of the process, and this is its weak point. Special practice, however, will enable the operator to hit the exact point closely.

---

[1] *J. A. C. S.*, 1895, 17, 346. Also, A. H. Low, *Technical Methods of Ore Analysis*.

Casamajor[1] uses instead of ammonia the alkaline tartrate solution of Fehling, adding a slight excess so as to make a clear blue solution. The addition of the sulphide gives an intense black-brown precipitate, the liquid being stirred vigorously till clear. The copper sulphide agglomerates into curds, and the reagent is added until no further action occurs with a drop of the sodium sulphide. This modification can also be used for lead. $PbSO_4$ is easily soluble in the tartrate solution, and can be determined by the sodium sulphide in the same way as copper.

The colour of the solution is not regarded, but the clotty precipitate of sulphide, which is easily made to agglomerate by vigorous stirring. Very good results may be gained by this modification.

Copper can also be first separated by glucose, or as thiocyanate (Rivot), then dissolved in HNO_3, and treated with the tartrate.

Precipitation in Acid Solution.—The copper solution is placed in a stoppered flask (400 or 500 c.c.), freely acidified with hydrochloric acid, then diluted with about 200 c.c. of hot water.

The alkali sulphide is then delivered in from a burette, the stopper replaced, and the mixture well shaken; the precipitate of copper sulphide settles readily, leaving the supernatant liquid clear; fresh sulphide solution is then added at intervals until no more precipitate is produced. The calculation is the same as in the case of alkaline precipitation, but the copper is precipitated as sulphide instead of oxysulphide.

6. Determination by Stannous Chloride (Weil).[2]

This process is based on the fact that a solution of a cupric salt in large excess of hydrochloric acid at a boiling heat shows, even when the smallest trace is present, a greenish-yellow colour. If to such a solution stannous chloride is added in minute excess, a colourless cuprous chloride is produced, and the loss of colour indicates the end of the process.

$$2CuCl_2 + SnCl_2 = Cu_2Cl_2 + SnCl_4.$$

The change is easily distinguishable by the eye, but should any doubt exist as to whether stannous chloride is in excess, a small portion of the solution may be tested with mercuric chloride. Any precipitate of calomel indicates the presence of stannous chloride.

The tin solution is prepared as described on p. 134.

A standard copper solution is made by dissolving pure copper sulphate in distilled water, in the proportion of 39·286 gm. per litre = 10 gm. of Cu.

Method of Procedure for Copper alone.—10 c.c. of the copper solution (= 0·1 gm. of Cu) are put into a white-glass flask, 25 c.c. of pure strong hydrochloric acid added, placed on a sand-bath and brought to boiling heat; the tin solution is then quickly delivered in from a burette until the colour is nearly destroyed, finally a drop at a time till the liquid is as colourless as distilled water. No oxidation will take place during the boiling, owing to the flask being filled with acid vapours.

---

[1] *C. N.*, 1882, **45**, 167.

[2] *Z. a. C.*, 1870, **9**, 297.

A sample of copper ore is prepared in the usual way by treatment with nitric acid, which is afterwards removed by evaporating with sulphuric acid. Silica, lead, tin, silver, or arsenic, are of no consequence, as when the solution is diluted with water to a definite volume, the precipitates of these substances settle to the bottom of the measuring flask, and the clear liquid may be taken out for titration. In case antimonic acid is present it will be reduced with the copper, but on exposing the liquid for a night in an open basin, the copper will be completely re-oxidized but not the antimony; a second titration will then show the amount of copper.

Method of Procedure for Ores containing Copper and Iron.—In the case of copper ores where iron is also present, the quantity of tin solution required will of course represent both the iron and the copper. In this case a second titration of the original solution is made with zinc and permanganate, and the quantity so found is deducted from the total quantity; the amount of tin solution corresponding to copper is thus found.

EXAMPLE: A solution was prepared from 10 gm. of ore and diluted to 250 c.c.; 10 c.c. required 26·75 c.c. of tin solution whose strength was 16·2 c.c. for 0·1 gm. of Cu.

10 c.c. of ore solution were diluted, zinc and platinum added, warmed till reduction was complete, and the solution titrated with permanganate, of which the quantity used = 0·0809 gm. of Fe.

The relative strength of the tin solution to iron is found thus:—

$$\begin{aligned} 63{\cdot}57 : 0{\cdot}1 &= 55{\cdot}84 : x \\ x &= {\cdot}08784 \\ \text{i.e., } 0{\cdot}1 \text{ gm. Cu} &= {\cdot}08784 \text{ gm. Fe.} \\ &= 16{\cdot}2 \text{ c.c. } SnCl_2. \end{aligned}$$

Again,

$$\begin{aligned} {\cdot}08784 : {\cdot}0809 &= 16{\cdot}2 : y \\ y &= 14{\cdot}92 \\ \text{i.e., } 0{\cdot}0809 \text{ Fe found above} &= 14{\cdot}92 \text{ c.c. } SnCl_2 \\ \text{Hence, iron + copper} &= 26{\cdot}75 \text{ c.c. } SnCl_3 \\ \text{Iron} &= 14{\cdot}92 \\ \hline \text{Copper} &\quad 11{\cdot}83 \end{aligned}$$

Finally,

$$\begin{aligned} 16{\cdot}2 : 11{\cdot}83 &= 0{\cdot}1 : z \\ z &= 0{\cdot}07302. \end{aligned}$$

That is, 10 c.c. of ore solution contain 0·07302 gm. Cu, or 250 c.c. (= 10 gm. of ore) contain $\cdot07302 \times \frac{100}{4} = 1{\cdot}825$ gm.

The percentage of copper is, therefore, 18·25.

A gravimetric determination as a control gave 18·34 per cent. Cu.

Fe determined volumetrically gave 20·25 per cent., gravimetrically 20·10 per cent.

The method is specially adapted for the technical analysis of fahl-ores.

7. Precipitation as Cuprous Thiocyanate, Volhard's Method.

The necessary standard solutions are described on p. 151. Each c.c. of $^{N}/_{10}$ thiocyanate represents 0·006357 gm. Cu.

$$2CuSO_4 + 2KSCN + SO_2 + 2H_2O = 2CuSCN + 2H_2SO_4 + K_2SO_4.$$

METHOD OF PROCEDURE: The copper in sulphuric or nitric acid solution is evaporated to remove excess of acid, or if the acid is small in quantity neutralized with sodium carbonate, washed into a 500 c.c. flask, and enough aqueous solution of SO_2 added to dissolve the traces of basic carbonate and leave a distinct smell of SO_2. Heat to boiling, and run in the thiocyanate from a burette until the addition produces no change of colour, add 3 or 4 c.c. more, and note the entire quantity used, allow to cool, fill to mark, and shake well. 100 c.c. are then filtered through a dry filter, 10 c.c. of ferric indicator with some nitric acid added, then titrated with $^{N}/_{10}$ silver nitrate till colourless: then again thiocyanate till the reddish colour appears. The volume of silver solution, less the final correction with thiocyanate, deducted from the original thiocyanate used, will give the volume of the latter required to precipitate the copper.

The process is not accurate in presence of Ag, Hg, Cl, I, Br, or As_2O_5. It is very doubtful whether the presence of *iron* makes any difference whatever in view of the fact that an appreciable amount of ferric salt is eventually added as indicator. Graham Edgar[1] has described a modification by which copper can be determined with accuracy in the presence of as much as three times its own weight of iron, both metals being determined in the same solution.

METHOD OF PROCEDURE: The solution, containing sulphuric acid, is nearly neutralized with ammonia or sodium carbonate, saturated with SO_2, heated to boiling, and a measured excess of standard ammonium thiocyanate solution added to precipitate the copper. The mixture is then boiled vigorously for 10 minutes in a current of CO_2, to remove SO_2, cooled, in the presence of CO_2, and filtered. The precipitate is washed with cold water, and the filtrate and washings, after adding sulphuric acid and excess of standard silver nitrate to remove the unused thiocyanate, are titrated with permanganate to determine the iron. The colour of the permanganate is removed by means of a trace of ferrous sulphate, and the excess of silver at once precipitated by titrating with standard thiocyanate. The copper is calculated from the difference between the total volume of thiocyanate used and that equivalent to the silver nitrate added.

Several modern processes for the volumetric determination of copper, chiefly due to American chemists, have been based upon the separation of the metal as cuprous thiocyanate. One (Fairlie's) has already been mentioned as a modification of the iodide method. In another (Meade's, see p. 202), the iron equivalent of the separated copper is titrated with permanganate. In all cases the precipitation as thiocyanate is effected as already described.

GARRIGUE'S ACIDIMETRIC METHOD.[2] The washed thiocyanate precipitate, with the filter, is decomposed by boiling with caustic alkali (see Meade's method, p. 202), excess of normal soda being used, and the excess, after filtering off the cuprous hydroxide, titrated by normal acid, with methyl orange as indicator. The method is said to be especially useful in alloy assay.

PARR'S PERMANGANATE METHOD.[3] The precipitated cuprous thiocyanate is decomposed by caustic alkali, the copper oxidized in alkaline solution by permanganate without decomposition of the alkali thiocyanate, and the thiocyanic acid titrated in acid solution with permanganate, the whole being effected in one operation as follows: The washed precipitate of cuprous thiocyanate and the asbestos pulp or filter paper are treated with 10 c.c. of a 10 per cent. solution of caustic potash and 10 c.c. of ammonia (sp. gr. 0·96), and then immediately titrated with permanganate until, upon warming to about 50° C., the green colour of the supernatant liquid remains. About one-third or one-fourth of the quantity of permanganate necessary for this is then run in, the mixture allowed to stand for 5 minutes, then acidified with 25 c.c. sulphuric acid (1 : 1 or 2) and titrated to a pink coloration with permanganate. 10 atoms of cuprous Cu are oxidized by 7 molecules of permanganate. The copper value of the latter is found by multiplying the iron factor by 0·1602.[1]

---

[1] *J. A. C. S.*, 1916, **38**, 884.

[2] *Ibid.*, 1897, **19**, 940.

[3] *Ibid.*, 1900, **22**, 685 and **24**, 580. See also Hawley, *Eng. and Mining J.*, 1908, 1155, and *J. S. C. I.*, 1909, **28**, 163.

IODATE METHOD.[2] The application of the potassium iodate method of Andrews (p. 138) has been found to afford a simple and accurate process for the titration of cuprous thiocyanate. The washed precipitate, together with the asbestos or filter-paper on which it was filtered, is placed in a bottle, 5 c.c. of chloroform, 20 c.c. of water, and 30 c.c. of hydrochloric acid are added, and a standard solution of potassium iodate, containing 11·784 gm. of the salt per litre, is run in with constant shaking, until the colour first formed in the chloroform disappears. The reaction proceeds according to the equation :—

$$4CuSCN + 7KIO_3 + 14HCl = 4CuSO_4 + 7KCl + 7ICl + 4HCN + 5H_2O.$$

One c.c. of the standard solution corresponds to 0·0020 gm. of copper. The chloroform may be used a second time.

To apply the method to *ores*, the sample is dissolved in nitric acid or aqua regia, and boiled down with sulphuric acid until fumes of the latter are given off. The residue is diluted and filtered after the addition of 1 or 2 drops of hydrochloric acid if silver is present. The small quantities of lead and antimony left in solution do not interfere with the subsequent precipitation of the copper by means of sulphur dioxide and ammonium thiocyanate. A complete determination can be made in one hour.

Potassium iodate can be obtained pure, and its solution is very stable.

8. Technical Examination of Copper Ores (Steinbeck's) Process.

In 1867 the Directors of the Mansfeld Copper Mines offered a premium for the best method of examining these ores, the chief conditions being tolerable accuracy, simplicity of working, and the possibility of one operator making at least eighteen assays in the day.

The fortunate competitor was Dr. Steinbeck, whose process completely satisfied the requirements. The whole report is contained in *Z. a. C.*, 1869, **8**, 1, and is also translated in *C. N.* 1869, **19**, 207. The following is a condensed account of the process, the final titration of the copper being accomplished by potassium cyanide as on p. 206. A very convenient arrangement for filling the burette with standard solution where a series of analyses has to be made, and the burette continually emptied, is shown in fig. 39; it may be refilled by simply blowing upon the surface of the liquid.

(*a*) **The Extraction of the Copper from the Ore.**—5 gm. of pulverized ore are put into a flask with from 40 to 50 c.c. of hydrochloric acid (specific gravity

---

[1] Compare Clark, *J. Ind. and Eng. Chem.* 1919, **11**, 1138.

[2] Jamieson, Levy, and Wells, *J. A. C. S.*, 1908, **30**, 760.

1·16), whereby all carbonates are converted into chlorides, while carbonic acid is expelled.

After a while there is added to the fluid in the flask 6 c.c. of a special nitric acid, prepared by mixing equal bulks of water and pure nitric acid of 1·42 sp. gr. As regards certain ores, however, specially met with in the district of Mansfeld. some, having a very high percentage of sulphur and bitumen, have to be roasted previous to being subjected to this process; and others, again, require only 1 c.c. of nitric acid instead of 6. The flask containing the assay is digested on a sand-bath for half an hour, and the contents boiled for about fifteen minutes; after which the whole of the copper occurring in the ore, and all other metals, are in solution as chlorides. The blackish residue, consisting of sand and schist, has been proved by numerous experiments to be either entirely free from copper, or to contain at the most only 0·01 to 0·03 per cent.

(*b*) **Separation of the Copper.**—The solution of metallic and alkaline earthy chlorides, and some free HCl, obtained as just described, is separated by filtration from the insoluble residue, and the fluid run into a covered beaker of about 400 c.c. capacity. In this beaker a rod of metallic zinc, weighing about 50 gm., has been previously placed, fastened to a piece of stout platinum foil. The zinc to be used for this purpose should be as free as possible from lead, and at any rate should not contain more than from 0·1 to 0·3 per cent. of the latter metal. The precipitation of the copper in the metallic state sets in during the filtration of the warm and concentrated fluid, and is, owing especially also to the entire absence of nitric acid, completely finished in from half to three-quarters of an hour after the beginning of the filtration. If the fluid be tested with SH_2 no trace of copper can or should be detected; the spongy metal partly covers the platinum foil, partly floats about in the liquid, and in case either the ore itself or the zinc applied in the experiment contained lead, small quantities of that metal will accompany the precipitated copper. After the excess of zinc (for an excess must always be employed) has been removed, the metal is repeatedly and carefully washed by decantation with fresh water, and care taken to collect together every particle of the spongy mass.

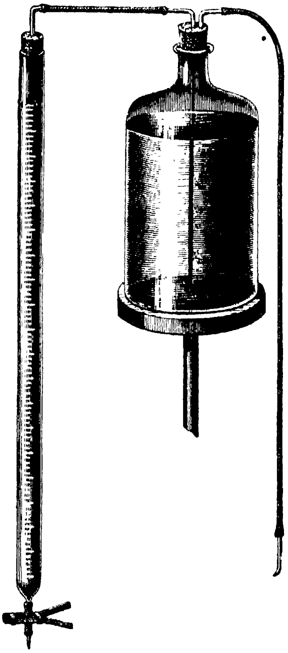

FIG. 39.

(*c*) **Determination of the Precipitated Copper.**—To the spongy metallic mass in the beaker, wherein the platinum foil is left, since some of the metal adheres to it, 8 c.c. of the special nitric acid are added, and the copper dissolved by the aid of moderate heat in the form of cupric nitrate, which, in the event of any small quantity of lead being present, will of course be contaminated with lead.

When copper ores are dealt with containing above 6 per cent. of copper, which may be approximately determined from the bulk of the spongy mass of precipitated metal, 16 c.c. of nitric acid, instead of 8, are applied for dissolving the metal. The solution thus obtained is left to cool, and next mixed, immediately before titration with cyanide, with 10 c.c. of special solution of liquid ammonia, prepared by diluting 1 volume of liquid ammonia (sp. gr. 0·93) with 2 volumes of distilled water.

The titration with cyanide is conducted as described on p. 207.

'In the case of such ores as yield over 6 per cent. of copper, and when a double quantity of nitric acid has consequently been used, the solution is diluted with water, and made to occupy a bulk of 100 c.c.; this bulk is then exactly divided into two portions of 50 c.c. each, and each of these separately mixed with 10 c.c. of ammonia, and the copper therein volumetrically determined. The deep blue coloured solution only contains, in addition to the copper compound, ammonium nitrate; any lead which might have been dissolved having been precipitated as hydrated oxide, which does not interfere with the titration with cyanide. The solution of the last-named salt is so arranged that 1 c.c. thereof indicates exactly 0·005 gm. of copper (about 21 gm. of the pure salt per litre). Since, for every assay, 5 gm. of ore have been taken, 1 c.c. of the titration fluid is equal to 0·1 per cent. of copper, it hence follows that, by multiplying the number of c.c. of cyanide solution used to make the blue colour of the copper solution disappear by 0·1, the percentage of copper contained in the ore is immediately ascertained.

Steinbeck tested this method specially, in order to see what influence is exercised thereupon by (1) ammonium nitrate, (2) caustic ammonia, (3) lead. Pure electrolytic copper was used for the experiments, ignited to destroy any organic matter which might accidentally adhere to it, and next cleaned by placing it in dilute nitric acid. 5 gm. of this metal were placed in a litre flask, and dissolved in 266·6 c.c. of special nitric acid, the flask gently heated, and, after cooling, the contents diluted with water, and made up to 1000 c.c. 30 c.c. of this solution were always applied to titrate one and the same solution of cyanide in all circumstances. When 5 gm. of ore, containing on an average 3 per cent. of copper, are taken for assay, that quantity of copper is exactly equal to 0·150 gm. of the chemically pure copper. The quantity of nitric acid taken to dissolve 5 gm. of pure copper (266·6 c.c.) was purposely taken, so as to correspond with the quantity of 8 c.c. of special nitric acid which is applied in the assay of the copper obtained from the ore, and this quantity of acid is the exact amount in 30 c.c. of the solution of pure copper.

The influence of double quantities of ammonium nitrate and free caustic ammonia (the quantity of copper remaining the same) is shown as follows:—

(*a*) 30 c.c. of the normal solution of copper, containing exactly 0·150 gm. of copper, were rendered alkaline with 10 c.c. of special ammonia, and were found to require, for entire decolorization, 29·8 c.c of cyanide. A second experiment, again with 30 c.c. of copper solution, and otherwise under identically the same conditions, required 29·9 c.c. of cyanide. The average is 29·85 c.c.

(*b*) When to 30 c.c. of the copper solution first 8 c.c. of special nitric acid are added, and then 20 c.c. of special ammonia instead of only 8, whereby the quantity of free ammonia and of ammonium nitrate is double what it was in the case of *a*, there is required of the same cyanide 30·0 c.c. to produce decolorization. A repetition of the experiment, under exactly the same conditions, gave 30·4 c.c. of the cyanide; the average is, therefore, 30·35 c c. The difference amounts to only 0·05 per cent. of copper, which may be allowed for in the final calculation.

When, however, large quantities of ammoniacal salts are present in the fluid to be assayed for copper by means of cyanide, and especially when ammonium carbonate, sulphate and, worse still, chloride are simultaneously present, these salts exert a very disturbing influence.[1] The presence of lead in the copper solution to be assayed has the effect of producing, on the addition of 10 c.c. of normal ammonia, a milkiness with the blue tint; but this does not at all interfere with the determination of the copper by means of the cyanide, provided the lead be not in great excess; and a slight milkiness of the solution even promotes the visibility of the approaching end of the operation.

Steinbeck made some experiments purposely to test this point, and his results show that a moderate quantity of lead has no influence.

Experiments were also carefully made to ascertain the influence of zinc, the result of which showed that up to 5 per cent. of the copper present, the zinc had no disturbing action; but a considerable variation occurred as the percentage increased above that proportion. Care must, therefore, always be taken in washing the spongy copper precipitated from the ore solution by means of zinc.

The titration must always take place at ordinary temperatures, since heating the ammoniacal solution while under titration to 40° or 45° C. considerably reduces the quantity of cyanide required.

9. Determination of Copper Colorimetrically.

This method can be adopted with very accurate results, as in the case of iron, and is available for slags, poor cupreous pyrites, waters, etc.[2]

The reagent used is the same as in the case of iron, viz., potassium ferrocyanide, which gives a purple-brown colour with very dilute solutions of copper. This reaction, however, is not so delicate as it is with iron, for 1 part of the latter in 13,000,000 parts of water can be detected by means of potassium ferrocyanide; while 1 part of copper in a neutral solution, containing ammonium nitrate, can only be detected in 2,500,000 parts of water. Of the coloured reactions which copper gives with different reagents, those with sulphuretted hydrogen and potassium ferrocyanide are by far the most delicate, both showing their respective colours in 2,500,000 parts of water.

Of the two reagents sulphuretted hydrogen is the more delicate; but potassium ferrocyanide has a decided advantage over sulphuretted hydrogen in the fact that lead, when not present in too large quantity, does not interfere with the depth of colour obtained, whereas to sulphuretted hydrogen it is, as is well known, very sensitive.[1]

---

[1] I have retained this technical process in its original form, notwithstanding the use of ammonia, because it is systematic, and the results obtained by it are all comparable among themselves Of course soda or potash may be used in place of ammonia, if the cyanide is standardized with them.

[2] Carnelly, *C. N.*, 1875, **32**, 308,

And though iron if present would, without special precaution being taken, prevent the determination of copper by means of ferrocyanide; yet, by the method described below, the amounts of these metals contained together in a solution can be determined by this reagent.

Ammonium nitrate renders the reaction much more delicate; other salts, as ammonium chloride and potassium nitrate, have the same effect.

The method of analysis consists in the comparison of the purple-brown colours produced by adding to a solution of potassium ferrocyanide—first, a solution of copper of known strength; and, second, the solution in which the copper is to be determined.

The solutions and materials required are as follows:—

(1) Standard copper solution.—Prepared by dissolving 0·3929 gm. of pure $CuSO_4, 5H_2O$ in 1 litre of water. 1 c.c. = 0·1 mgm. Cu.

(2) Solution of ammonium nitrate.—Made by dissolving 100 gm. of the salt in 1 litre of water.

(3) Potassium ferrocyanide solution—1 : 25.

(4) Two glass cylinders holding rather more than 150 c.c. each, the point equivalent to that volume being marked on the glass. They must both be of the same tint, and as colourless as possible.

A burette, graduated to $\frac{1}{10}$ c.c. for the copper solution; a 5 c.c. pipette for the ammonium nitrate; and a small tube to deliver the ferrocyanide in drops.

METHOD OF PROCEDURE: Five drops of the potassium ferrocyanide are placed in each cylinder, and then a measured quantity of the neutral solution in which the copper is to be determined is added to one of them, and both filled up to the mark with distilled water, 5 c.c. of the ammonium nitrate solution added to each, and then the standard copper solution run gradually into the other till the colours in both cylinders are of the same depth, the liquid being well stirred after each addition. The number of c.c. used is then read off. Each c.c. corresponds to 0·1 mgm. of copper, from which the amount of copper in the solution in question can be calculated.

The solution in which the copper is to be determined must be neutral; for if it contain free acid the latter lessens the depth of colour, and changes it from a purple-brown to an earthy-brown. If it should be acid, it is rendered slightly alkaline with ammonia, and the excess of the latter got rid of by boiling. The solution must not be alkaline, as the brown coloration is soluble in ammonia and decomposed by potash or soda; if it be alkaline from ammonia, this is remedied as before by boiling it off; while free potash or soda, should they be present, are neutralized by an acid, and the latter by ammonia.

Lead, when present in not too large quantity, has little or no effect on the accuracy of the method. The precipitate obtained on adding potassium ferrocyanide to a lead salt is white; and this, except when present in comparatively large quantity with respect to the copper, does not interfere with the comparison of the colours.

---

[1] In colour titrations of this character it is essential that the comparisons be made under the same circumstances as to temperature, dilution, and admixture of foreign substances, otherwise serious errors will arise.

When copper is to be determined in a solution containing iron, the following method is adopted :—

A few drops of nitric acid are added to the solution in order to oxidize the iron, the liquid evaporated to a small bulk, and the iron precipitated by ammonia. Even when very small quantities of iron are present, this can be done easily and completely if there be only a very small quantity of fluid. The precipitate of ferric oxide is then filtered off, washed once, dissolved in nitric acid, and reprecipitated by ammonia, filtered and washed The iron precipitate is now free from copper, and in it the iron can be determined by dissolving in nitric acid, making the solution nearly neutral with ammonia, and determining the iron by the method on p. 245. The filtrate from the iron precipitate is boiled till the ammonia is completely driven off, and the copper determined in the solution so obtained as already described.

When the solution containing copper is too dilute to give any coloration directly with ferrocyanide, a measured quantity of it must be evaporated to a small bulk, and filtered if necessary; and if it contain iron also, treated as already described.

In the **determination of copper and iron in water,** for which the method is specially applicable, a measured quantity is evaporated to dryness with a few drops of nitric acid, ignited to get rid of any organic matter that might colour the liquid, dissolved in a little boiling water and a drop or two of nitric acid; if it is not all soluble it does not matter. Ammonia is next added to precipitate the iron, the latter filtered off, washed, redissolved in nitric acid, and again precipitated by ammonia, filtered off, and washed. The filtrate is added to the one previously obtained, the iron determined in the precipitate, and the copper in the united filtrates.

10. Determination by Titration of Copper Ferrocyanide with Potassium Cyanide.

Sanchez[1] has devised the following process, which is applicable in presence of tin, arsenic, antimony and organic acids, but iron, lead, zinc, nickel, cobalt, manganese, and ammonium salts must be absent The method is based on the fact that when copper ferrocyanide is dissolved in a solution of potassium cyanide a very sharp change of colour accompanies the reaction, which is as follows :—

$$Cu_2FeCy_6 + 6KCy = K_4FeCy_6 + 2(CuCy_2, KCy).$$

The solution must be exactly neutral.

Method of Procedure: The nitric acid solution of copper is first evaporated to dryness with sulphuric acid, any lead sulphate filtered off after adding cold water to the residue, and the copper is precipitated as Cu_2S by acidifying with H_2SO_4 and boiling with 10-20 c.c. of a 50 per cent. solution of sodium thiosulphate. The precipitate is washed with boiling water, dissolved in nitric acid, the excess of acid boiled off, and the solution made up to a known volume. An aliquot portion of this is titrated with standard alkali, using methyl orange as indicator (or phenolphthalein when organic acids are present), and the amount of alkali found is added to another such portion, potassium ferrocyanide added, and the titration with potassium cyanide then proceeded with. The standard cyanide solution (6·5 gm. KCy per litre) is standardized against a solution containing 1 gm. of copper per litre. To 10 c.c. of the latter solution 1 c c. of a 10 per cent. solution of potassium ferrocyanide is added, and the cyanide solution is carefully run in from a burette until the reddish-brown colour suddenly changes to greenish-yellow.

---

[1] *Bull. Soc. Chim.*, 1910, 7, 9.

CYANOGEN.

CN = 26·01

1 c.c. $^{N}/_{10}$ silver solution = 0·005202 gm. Cyanogen.
„ „ = 0·005404 gm. Hydrocyanic acid.
„ „ = 0·013022 gm. Potassium cyanide.
„ $^{N}/_{10}$ iodine solution = 0·003255 gm. Potassium cyanide.

1. By Standard Silver Solution (Liebig).

THIS ready and accurate method of determining cyanogen in hydrocyanic acid, alkali cyanides, etc., was discovered by Liebig, and is fully described in *Ann. der Chem. und Pharm.*, lxxvii. 102. It is based on the fact that when a solution of silver nitrate is added to an alkali solution containing cyanogen, with constant stirring, no permanent precipitate of silver cyanide appears until all the cyanogen has combined with the alkali and the silver to form a soluble double salt (in the presence of potash, for example, KCy, AgCy). If the slighest excess of silver, over and above the quantity required to form this combination, be added, a permanent precipitate of silver cyanide is produced, the double compound being destroyed. If, therefore, the silver solution be of known strength, the quantity of cyanogen present is easily found ; 1 eq. of silver in this case being equal to 2 eq. cyanogen.

So fast is this double combination that, when sodium chloride is present, no permanent precipitate of silver chloride is produced until the quantity of silver necessary to form the compound is slightly overstepped.

Siebold, however, has pointed out that this process, in the case of free hydrocyanic acid, is liable to serious errors unless the following precautions are observed :—

(*a*) The solution of sodium or potassium hydrate should be placed in the beaker first, and the hydrocyanic acid added to it from a burette dipping into the alkali. If, instead of this, the acid, is placed in the beaker first, and the alkali hydrate added afterwards, there may be a slight loss by evaporation, which becomes appreciable whenever there is any delay in the addition of the alkali.

(*b*) The mixture of hydrocyanic acid and alkali should be largely diluted with water before the silver nitrate is added. The most suitable proportion of water is from ten to twenty times the volume of the officinal or of Scheele's acid. With such a degree of dilution, the final point of the reaction can be observed with greater precision.

(*c*) The amount of alkali used should be as exactly as possible that required for the conversion of the hydrocyanic acid into alkali cyanide, as either an insufficiency or an excess affects the accuracy of the result. It is advisable to make first a rough estimation with excess of soda as a guide, then finish with a solution as neutral as possible. As a guide to the neutrality, or rather the slight amount of alkalinity of the solution, a little Poirrier's Blue C_4B may be used as indicator. This gives a red colour with alkali hydroxides, but is not acted upon by HCy or alkali cyanides.

The volume taken for titration should not contain more than 0·1 gm. HCN. For this quantity use 5 c.c. $^N/_1$ alkali and 0·5 gm. sodium bicarbonate. Titrate over black paper. This method is useless for the determination of cyanogen in double cyanides and in mercuric cyanide.

For the *determination of cyanide in presence of chloride*, proceed as follows:—

Determine the cyanide by Liebig's method, add more than enough standard silver nitrate solution to combine with the chloride, acidify with nitric acid, make up to a definite volume, filter through a dry filter, and titrate the excess of silver in an aliquot portion of the filtrate by Volhard's method.

A modification suggested by Guerin,[1] in which the hydrocyanic acid is neutralized by borax, has the advantage that excess of borax does not interfere.

If ferrocyanide or thiosulphate be present, a crystal or two of potassium iodide should be added before the titration with silver nitrate.[2] The precipitate then consists of silver iodide, of which 1 eq. = 2 eq. of cyanide as with silver nitrate. The end-point of the titration is sharper.

Caution.—In using the pipette for measuring hydrocyanic acid, it is advisable to insert a plug of cotton wool, slightly moistened with silver nitrate, into the upper end, so as to avoid the danger of inhaling any of the highly poisonous acid; otherwise it is decidedly preferable to weigh it.

2. By Standard Mercuric Chloride (Hannay).

This convenient method is fully described by the author,[3] and is well adapted for the technical examination of commercial cyanides, etc., giving good results in the presence of cyanates, sulphocyanates, alkali salts, and compounds of ammonia and silver.

The standard solution of mercury is made by dissolving 13·537 gm. $HgCl_2$ in water, and diluting to a litre. Each c.c. = 0·00651 gm. of potassium cyanide or 0·002611 gm. Cy.

METHOD OF PROCEDURE: The cyanide is dissolved in water, and the beaker placed upon black paper or velvet; ammonia is then added in moderate quantity, and the mercuric solution cautiously added with constant stirring until a bluish white opalescence is permanently produced.

---

[1] *J. Pharm. Chim.* 1905, **22**, 433; *Analyst*, 1906, **31**, 27

[2] *Treadwell, Z. anorg. Chem.* 1911, **71**, 219.

[3] *J. C. S.*, 1878, 245.

With pure substances the reaction is very delicate, but not so accurate with impure mixtures occurring in commerce.

3. By Iodine (Fordos and Gelis).

This process, which is principally applicable to alkali cyanides, depends on the fact that when a solution of iodine is added to one of potassium cyanide the colour of the iodine solution is discharged so long as any undecomposed cyanide remains. The reaction may be expressed by the following equation :—

$$KCN + I_2 = KI + ICN.$$

Therefore, 2 eq. iodine represent 1 eq. cyanogen in combination; so that 1 c.c. of $^{N}/_{10}$ iodine expresses the half of $\frac{1}{10000}$ eq. cyanogen or its compounds. The end of the reaction is known by the yellow colour of the iodine solution becoming permanent. Starch indicator must not be used.

Commercial cyanides are, however, generally contaminated with caustic or monocarbonate alkalies, which would destroy the colour of the iodine like the cyanide; consequently these must be converted into bicarbonates, which is best done by adding carbonic acid water (ordinary soda water).

Example: 5 gm. of potassium cyanide were weighed and dissolved in 500 c.c. water; then 5 c.c. (= 0·05 gm. cyanide) taken with a pipette, diluted with about ¼ litre of water, 100 c.c. of soda water added, then $^{N}/_{10}$ iodine delivered from the burette until the solution possessed a slight but permanent yellow colour: 12·75 c.c. were required, which multiplied by 0·003255 gave 0·0415 gm. or 83 per cent. real cyanide. Sulphides must of course be absent.

Note.—Instead of adding "soda water" Drs. Henry and Auld[1] recommend the addition of a slight excess of sodium bicarbonate before titration with standard iodine solution.

4. By $^{N}/_{10}$ Silver Solution and Chromate Indicator.

Vielhaber[2] has shown that weak solutions of prussic acid, such as bitter-almond water, etc., may be readily titrated by adding magnesium hydrate suspended in water until alkaline, adding a drop or two of chromate indicator, and delivering in $^{N}/_{10}$ silver until the red colour appears, as in the case of titrating chlorides. 1 c.c. silver solution = 0·002702 gm. HCy.

This method may be found serviceable in the examination of opaque solutions of hydrocyanic acid, such as solutions of bitter-almond oil, etc.; but of course the absence of chlorine must be ensured, or, if present, the amount must be allowed for.

It is preferable to add the HCy solution to a mixture of magnesia and chromate, then immediately to titrate with silver.

FERRO- AND FERRI-CYANIDES.

Potassium Ferrocyanide.

$$K_4FeCy_6, 3H_2O = 422{\cdot}348.$$

Metallic iron × 7·563 = Crystallized Potassium ferrocyanide.
Ferrous ammonium sulphate × 1·080 = " " "

---

[1] *J. S. C. I.*, 1908, **27**, 429.

[2] *Arch. Pharm.* [3], **13**, 408.

Oxidation to Ferricyanide by Permanganate (De Haen).

Ferrocyanide may be determined by potassium permanganate, by which it is converted into ferricyanide. The process is easy of application, and the results accurate. A standard solution of pure ferrocyanide should be used as the basis upon which to work, but may be dispensed with, if the operator chooses to calculate the strength of his permanganate from iron or its compounds. If the permanganate is decinormal, there is, of course, very little need for calculation (1 eq. = 422·348 must be used as the systematic number, and therefore 1 c.c. of $^N/_{10}$ permanganate is equal to 0·042235 gm. of yellow prussiate). The standard solution of pure ferrocyanide contains 20 gm. in the litre: each c.c. will therefore contain 0·02 gm.

METHOD OF PROCEDURE:[1] This method is found to give accurate results when carried out as follows: 20 c.c. of sulphuric acid (1 : 1) are added to 150 to 200 c.c. of the solution (containing about 1 gm. of ferrocyanide), and the mixture is titrated with $^N/_{20}$ permanganate, until the colour changes from yellowish-green to yellowish-red. Hydroferricyanic acid may also be determined by permanganate, after reduction with ferrous sulphate; but this acid is preferably determined by Mohr's method (see below), which is accurate when carried out in the following manner: 0·7 gm. of ferricyanide is dissolved in about 50 c.c. of water, and to the neutral solution are added 3 gm. of potassium iodide and 1·5 gm. of zinc sulphate (free from iron); the solution is then shaken and titrated with $^N/_{20}$ thiosulphate. The determination of hydroferrocyanic acid by oxidation with iodine and titration with thiosulphate in the presence of alkali bicarbonate (Rupp and Schiedt; *J. S. C. I.*, 1902, **21**, 1099), is found to be inaccurate.

Determination of Ferrocyanides by means of Permanganate.

B. Campbell's[2] method is based on the fact that the ferrocyanogen complex is completely broken down by heating with sulphuric acid, and the iron salt, after reduction to the ferrous state, is then titrated with permanganate.

Reagents required.—(i) Sulphuric acid, made by diluting 5 volumes of the concentrated acid with 1 volume of water.

(ii) Decinormal solution of potassium permanganate.

METHOD OF PROCEDURE: 1·5 to 2 gm. of the finely powdered ferrocyanide are introduced into a conical flask by means of a funnel. The smallest possible quantity of water is used to rinse the funnel into the flask, and then at least 30 c.c. of sulphuric acid (i) are added, acid of this strength preventing the formation of white scales of anhydrous ferric sulphate, which are very sparingly soluble in water and sulphuric acid. The flask is then heated over a small rose flame until the solution becomes quiescent. After cooling and diluting, 5 gm. of zinc (free from iron, or of known iron content) are added. When the whole of the zinc has dissolved and the iron is completely reduced to the ferrous state, the funnel is rinsed into the flask and the solution titrated with N/10 permanganate solution.

---

[1] E. Muller and O. Diefenthaler, *Z. anorg. Chem.*, 1910, **67**, 418-436; also, Mecklenburg, *Z. a. C.*, 1910, **49**, 322, and *J. S. C. I.*, 1910, **29**, 946

[2] *Analyst*, 1915, **40**, 327

1 c.c. N/10 potassium permanganate = 0·0422 gm. K_4FeCy_6, $3H_2O$ or
0·0484 gm. Na_4FeCy_6, $10H_2O$.

A "blank" experiment with 10 gm. of the zinc used should be made with N/100 permanganate and one-twentieth of the number of c.c. required deducted from the burette readings in actual experiments.

The method is said to be of special value in determining the degree of purity of ferrocyanides containing carbonate or sulphate. Excellent results are recorded. The method is not suitable for the analysis of crude products, as these, quite apart from the frequent presence of complex iron cyanogen derivatives other than ferrocyanides, almost invariably contain iron which is not combined with cyanogen.

Commercial Ferrocyanides.

Potassium ferrocyanide, $K_4Fe(CN)_6$, $3H_2O$ = 422·36.
Sodium „ $Na_4Fe(CN)_6$, $10H_2O$ = 484·06.
Calcium „ $Ca_2Fe(CN)_6$, $12H_2O$ = 508·232.

All of the above are obtained as by-products in the coal-gas industry from the hydrocyanic acid present in the crude gas. The crude products in each case may consist of the soluble potassium, sodium, or calcium salt, but usually there are also present insoluble ferrocyanides in the form of double ferrocyanides of iron with these metals or ammonium, the amount of which has to be included in the analytical results. The products obtained from crude coal-gas frequently contain, in addition, appreciable quantities of the very soluble carbonyl ferrocyanide, $Na_3FeCO(CN)_5$, or sodium ferrocyanide, $Fe(CN)_2$, 4NaCN, in which one molecule of NaCN has been replaced by the radicle CO. In other cases, such as the spent oxide from gas-works, the whole of the ferrocyanide present is in an insoluble form and, before analysis, must be converted into soluble salts. This is done as follows:—

The sample is ground, thoroughly mixed, and a weighed portion (30 to 40 gm.) put into a mortar, caustic soda in excess and about 100 cc. of water added, and allowed to stand for several hours, with frequent trituration with the pestle. A few crystals of ferrous sulphate may also be added, to bring about the conversion of any cyanide present into ferrocyanide and the reduction of any ferricyanide to ferrocyanide. Heat should not be employed, as the products mostly contain both ammonia and sulphides or free sulphur, the latter yielding sodium sulphide by the action of the NaOH, and in hot solution the alkali sulphides, in presence of ammonia, effect a partial conversion of the ferrocyanide into sulphocyanide, thus tending to make the ferrocyanide results low. In absence of ammonia, however, boiling sodium sulphide has but little action on ferrocyanide. The mixture, when decomposition is complete, is either filtered and made up to 1 litre or it may be at once placed in a litre flask, made up to the mark, and a further addition of water made equal to the volume of the insoluble matter present: the whole is then well shaken, allowed to settle, and the clear solution taken for analysis.

Owing to the frequent presence of sulphocyanides and other oxygen-consuming bodies in the above products the old method of titration by standard permanganate is inadmissible and the two following methods are now recommended :—

1. Determination of the amount of hydrocyanic acid present (Feld).

2. Direct determination of the ferrocyanide present by titration with standard zinc or copper sulphate solution (Knublauch).

The first method is described by Dr. H. G. Colman[1] as the one giving the most accurate results, and is carried out as follows :—

A quantity of the solution, prepared as described above, and containing the equivalent of 0·3 to 0·5 gm. of K_4FeCy_6, is diluted with water in a large flask, mixed with 10 c.c. $^{N}/_{1}$ caustic soda, and heated to boiling: to this 15 c.c. of hot magnesium chloride solution (610 gm., $MgCl_2$, $6H_2O$ per litre) are added slowly with continual shaking in order to get a milky precipitate of magnesium hydrate, and the boiling continued for 5 minutes and no more—the object being to convert any free alkali into magnesium hydroxide. (If free cyanide is also present, the HCN in this form is then evolved, and may be condensed and collected for analysis, the boiling in that case being continued for a longer period.) 100 c.c. of boiling mercuric chloride solution (27·1 gm. $HgCl_2$ per litre) are then added, and the boiling continued for a further 10 minutes, all ferrocyanide being thus converted into mercuric cyanide. The flask is then connected to a condenser, 30 c.c. of 4N sulphuric acid added by means of a stoppered funnel, and distillation continued for 20 to 30 minutes, the end of the condenser dipping under the surface of 25 c.c. of $^{N}/_{10}$ NaOH placed in the receiver. The solution of sodium cyanide thus obtained is now diluted to about 400 c.c., a crystal of KI added, and $^{N}/_{10}$ silver nitrate run in from a burette until a permanent yellow precipitate of AgI is obtained.

$$1 \text{ c.c. } ^{N}/_{10}\ AgNO_3 = 0{\cdot}005404 \text{ gm. } HCN$$

and from this the amount of ferrocyanide is readily calculated.

Knublauch's method consists in titrating the ferrocyanide solution, acidified with sulphuric acid, with a standard solution of copper or zinc sulphate, using a ferric salt as indicator. If the solution contains sulphide, this is first removed by shaking with lead carbonate and filtering off the lead sulphide and the excess of lead carbonate. In order to obtain accurate results, it has been stated to be necessary to standardize the zinc or copper solution with the same salt of ferrocyanic acid as is used for the titration, owing to the influence of the soluble sulphate formed during the process. Dr. Colman[2] has shown, however, that, if the ferrocyanide present is not potassium ferrocyanide, by adding 50 c.c. of a cold saturated solution of potassium sulphate before titration (and the same quantity to the pure potassium ferrocyanide solution when standardizing the copper or zinc solution) excellent results are obtained. He uses standard solutions containing 10 gm. crystallized copper sulphate or (its exact equivalent) 11·51 gm. of crystallized zinc sulphate per litre. A standard solution of 4 gm. crystallized potassium ferrocyanide per litre, equal to 2·044 gm. ferrocyanic acid $H_4Fe(CN)_6$, may be used, 50 c.c. being taken for standardizing. The end-point of the titration is determined either by filtering small portions of the liquid through Swedish filter-paper and adding ferric solution to the filtrate, or placing a drop of the liquid on a drop-reaction filter paper, followed by a drop of ferric chloride so placed as to come in contact with the clear wetted portion only of the first spot. The titration should be carried out in a good light. The amount of dilution and degree of acidity, within reasonable limits, affect the result but little.

---

[1] *Analyst*, 1908, **33**, 261; 1910, **35**, 295.

[2] *Loc. cit.*

Dr. Skirrow[1] recommends stronger solutions than those given above. He uses solutions of 50 gm. crystallized sodium ferrocyanide and 46·5 gm. of zinc sulphate per litre, and in making a test always acidifies with 2 c.c. of dilute H_2SO_4 (1 : 2). He states that with the more concentrated solutions a sharper end-point is obtained and that the effect of the presence of excess of alkali sulphate is minimized.

The presence of carbonyl ferrocyanide interferes with the analysis in both of the methods described above, as it is precipitated along with the ferrocyanide by both zinc and copper solutions, and the hydrocyanic acid from it is determined along with the rest by the Feld method. Dr. Colman uses a simple method of separation based on the fact that the carbonyl ferrocyanides are readily soluble in dilute alcohol whilst ferrocyanides are insoluble. To the solution of ferrocyanides, which must be alkaline or neutral, four or five times its volume of methylated spirit (industrial alcohol) is added, the mixture is allowed to stand for several hours, and filtered. The precipitate is washed with a little methylated spirit and dried in the water oven. The filter paper and precipitate are then transferred to the titrating basin, water added, the liquid acidified, and then proceeded with as described above, or simply dissolved in water and treated by the Feld process.

Determination of Ferrocyanides.

H. E. Williams's method.[2]—This method is applicable to any ferrocyanides, soluble or insoluble, also to the sparingly soluble double ferrocyanides, such as those of calcium, potassium, magnesium, ammonium, etc. Briefly, the method consists of the distillation of the ferrocyanide to be determined with a little cuprous chloride and a dilute acid, when the whole of the cyanogen contents of the ferrocyanide are driven off as hydrocyanic acid, which is absorbed by caustic alkali solution and then titrated with standard silver nitrate solution.

THE PROCESS (*a*) **For Ferrocyanides.** Dissolve 0·5 gm. of the ferrocyanide in 100 c.c. of water and transfer to a 250 to 300 c.c. distilling flask, add 0·05 to 0·1 gm. of cuprous chloride, dissolved in a few drops of HCl or a saturated solution of NaCl or KCl; gently shake the flask to mix the constituents, and then add 25 to 30 c.c. of 4N . H_2SO_4. The mixture is then distilled through a condenser into absorption flasks containing NaOH or KOH. After about half an hour's boiling the operation will be complete and the whole of the cyanogen in the absorption flasks. The latter are then emptied into a beaker, flasks and condenser washed out with distilled water, and the cyanide determined in the usual way with $^N/_{10}$ $AgNO_3$ solution. (*Note.*—It is advisable to wash the cuprous chloride with a little dilute H_2SO_4 before adding to the ferrocyanide, to remove any cupric chloride usually present on the commercial article.)

---

[1] *J. S. C. I.*, 1910, **29**, 319.

[2] *Ibid.*, 1912, **31**, 468.

Larger quantities of the ferrocyanide may be used if desired, in which case very little more (2 to 3 per cent. of the ferrocyanide taken) cuprous chloride will be required. It is well to remember, however, the extremely poisonous nature of HCN, and the fact that a dilute solution of cyanide is required for titration.

(*b*) **For Insoluble Ferrocyanides.** If the sample is in the dry state, it must first be ground to a fine powder before adding to the still, and in the case of ferric ferrocyanide, such as Prussian blue, more cuprous chloride than the amount mentioned above should be added. All that is necessary is to add 0·5 gm. of the finely powdered ferrocyanide to the still, with about 100 c.c. of water and the requisite quantity of acid and cuprous chloride.

(*c*) **For cyanogen mud or spent oxide** (products of the purification of coal gas). The sample is first carefully dried at 60° C., at which temperature no HCN is lost, extracted by CS_2 (best in a Soxhlet tube) to remove all free sulphur, then boiled with caustic soda or potash, filtered, washed to a definite volume, and a portion of the liquid is distilled with cuprous chloride and sulphuric acid as in (*a*). Should thiocyanates be present an extra amount of cuprous chloride should be added sufficient to precipitate them.

Potassium Ferricyanide.

$$K_6Fe_2Cy_{12} = 658·4.$$

Metallic iron	×	5·895	=	Potassium ferricyanide.
Ferrous ammonium sulphate	×	1·684	=	„ „
$^N/_{10}$ Thiosulphate	×	0·03292	=	„ „

By Iodine and Thiosulphate.

This salt can be determined either by reduction to ferrocyanide and titration with permanganate or dichromate, or by Lenssen's[1] method, which is based upon the fact that when potassium iodide and ferricyanide are mixed with tolerably concentrated hydrochloric acid iodine is set free.

$$K_6Fe_2Cy_{12} + 2KI = 2K_4FeCy_6 + I_2$$

the quantity of which can be determined by $^N/_{10}$ thiosulphate and starch. This method does not, however, give the most satisfactory results, owing to the variation produced by working with dilute or concentrated solutions, the reaction being reversible. The modification given under Zinc, is, however, more accurate, and is as follows: The ferricyanide is dissolved in a convenient quantity of water, potassium iodide in crystals added, together with hydrochloric acid in tolerable quantity, then a solution of pure zinc sulphate in excess; after standing a few minutes to allow of complete decomposition, the excess of acid is slightly over-neutralized by addition of sodium carbonate.

At this stage all the zinc ferricyanide first formed is converted into the ferrocyanide of that metal, and an equivalent quantity of iodine set free, which can at once be titrated with $^N/_{10}$ thiosulphate and starch, and with very great exactness.

---

[1] *Ann. Chem.*, **91**, 240; *ibid.* (Mohr), **105**, 60.

1 c.c. $^N/_{10}$ thiosulphate = 0·03292 gm. potassium ferricyanide.

Another method consists in boiling with excess of potash, then cooling, and adding H_2O_2 till the colour becomes yellow. The excess of the peroxide is then boiled off, H_2SO_4 added, and the solution titrated with permanganate.

Reduction of Ferri- to Ferro-cyanide.

This process is, of course, necessary when the determination by permanganate has to be made, and is best effected by boiling the weighed ferricyanide with an excess of potash or soda, and adding small quantities of concentrated solution of ferrous sulphate until the precipitate which is formed possesses a blackish colour (signifying that the magnetic oxide is formed). The solution is then diluted to a convenient quantity, say 300 c.c., well mixed, and filtered through a dry filter; 50 or 100 c.c. may then be taken, sulphuric acid added, and titrated with permanganate as before described.

Kassner[1] suggests the use of sodium peroxide for the reduction of ferri- to ferro-cyanide as being rapid and complete. About 0·5 gm. in 100 c.c. water requires about 0·06 gm. of the peroxide; the mixture is heated till all effervescence is over, acidified with sulphuric acid, cooled, and titrated with permanganate in the usual way.

THIOCYANATES.

Volhard's method is described on p. 150.

For the determination of thiocyanic acid in combination with the alkali or earthy bases, Barnes and Liddle[2] have devised a method which is easy of application, and gives good technical results. It is not, however, available for gas liquors.

The method depends upon the fact that when a solution of a cupric salt is added to a solution of a thiocyanate in presence of a reducing agent, as sodium bisulphite, the insoluble cuprous salt of thiocyanic acid is precipitated, the end of the reaction being ascertained by a drop of the solution in the flask giving a brown coloration when brought in contact with a drop of ferrocyanide. The following reactions take place:—

$$2CuSO_4 + 2KSCN + Na_2SO_3 + H_2O = 2CuSCN + K_2SO_4 + 2NaHSO_4$$

and

$$2CuSO_4 + Ba(SCN)_2 + Na_2SO_3 + H_2O = 2CuSCN + BaSO_4 + 2NaHSO_4.$$

The following solutions are required:—

1. A standard solution of copper sulphate containing 6·2430 gm. per litre, 1 c.c. of which is equivalent to 0·00145 gm. SCN.
2. A solution of sodium bisulphite of specific gravity 1·3.
3. A solution of potassium ferrocyanide (1 : 20).

Method of Procedure: About 3 gm. of the sample are weighed from a stoppered tube into a litre flask, dissolved in water, and made up to the mark. After well mixing, 25 c.c. are measured into a flask, about 3 c.c. of the bisulphite added, and the whole boiled. Whilst this is heating a burette is filled with the copper solution, and a white porcelain slab is spotted over with the ferrocyanide. When the liquid in the flask has reached the boiling point, 20 c.c. of the copper solution are run in, well shaken, the precipitate allowed to settle for about a minute, a drop is taken out by means of a glass rod, and brought in contact with a drop of ferrocyanide, and should no brown coloration appear, more of the copper solution is run in, say 1 c.c. at a time, and again tested. This is continued until a drop gives a colour immediately. By this means an approximation to the truth is obtained. It will be observed during a titration that the mixed drops, after standing for a minute, or even less, produce a brown tint. It is of the utmost importance that the coloration be *immediate*.

---

[1] *Arch. Pharm.*, **232**, 226.

[2] *J. S. C. I.*, 1883, **2**, 122.

A second 25 c.c. of the thiocyanate solution are run into a clean flask, the bisulphite added, and boiled as before.

Suppose that in the first experiment, after an addition of 27 c.c. of copper solution, no colour was formed with ferrocyanide, but that 28 c.c. gave an immediate colour; then in the second experiment 27 c.c. are run in at once, and the liquid is again tested, when no colour should appear. The copper solution is then run in drop by drop until there is a slight excess of copper, as proved by the delicate reaction with the ferrocyanide. The second experiment is thus rendered more exact by the experience gained in the first.

According to Schröder,[1] thiocyanates can be determined by means of permanganate, the reaction being approximately quantitative according to the equation:—

$$HSCN + O_2 = SO_2 + HCN$$

when $^N/_{10}$ solutions are employed and when the manganese is precipitated by sodium carbonate, redissolved in HCl and again titrated. A correct determination of thiocyanic acid may, however, be made by adding a definite volume of the thiocyanate solution to a known excess of warmed permanganate solution acidified with sulphuric and phosphoric acids, decomposing the excess of permanganate by the addition of an excess of either standardized oxalic acid solution or hydrogen peroxide, and titrating the latter with permanganate.

For the determination of thiocyanates and ferrocyanides, etc., in cyanide solutions containing copper, see Green.[2]

Determination of Thiocyanate in the Presence of Cyanide.—Determine the cyanide by Liebig's method, add more than enough standard silver solution to combine with the thiocyanate, acidify with nitric acid, make up to a definite volume, filter through a dry filter, and titrate the excess of silver in an aliquot portion of the filtrate by Volhard's method.

---

[1] *J. S. C. I.*, 1909, **28**, 1066.

[2] *Ibid.*, 1908, **27**, 1085.

GOLD.

Au = 197·2.

1 c.c. of normal oxalic acid = 0·0657 gm. Gold.

THE technical assay of gold for coining purposes is invariably performed by cupellation. Trichloride of gold is, however, largely used in photography and electro-gilding, and therefore it may be necessary sometimes to ascertain the strength of a solution of the chloride, or its value as it occurs in commerce.

If to a solution of gold in the form of chloride (free from nitric acid and the free hydrochloric acid nearly neutralized by ammonia) an excess of oxalic acid be added, in the course of from 18 to 24 hours all the gold will be precipitated in the metallic form, while the corresponding quantity of oxalic acid has been dissipated in the form of carbonic acid; if, therefore, the quantity of oxalic acid originally added be known, and the excess, after complete precipitation of the gold, be found by permanganate, the amount of gold can be ascertained.

A more rapid method consists in boiling the neutral gold solution with an excess of standard solution of potassium oxalate containing 8·3 gm. of the pure salt per litre, and titrating back with a permanganate solution which has the same working strength as the oxalate. Each c.c. of oxalate solution decomposed represents 0·00657 gm. Au.

The determination of small proportions of gold in solution can be done by iodine and thiosulphate as shown by Petersen,[1] and the method has been verified by F. A. Gooch and F. H. Morley.[2] These chemists found that the reduction of the auric salt with the consequent liberation of iodine was somewhat influenced by the volume of the solution, the amount of iodine present, and the time of action. Their experiments showed that the best effects were obtained in a solution of pure gold chloride of about 0·8 gm. of the salt to the litre by using 0·1 gm. KI to volumes of the chloride ranging between 25 and 50 c.c. The iodine and thiosulphate solutions used were about $^N/_{100}$ strength and verified against each other. The solution of KI contained 10 gm. per litre.

METHOD OF PROCEDURE: The gold solution is measured from a burette and the potassium iodide added in the proportion above mentioned; there must always be more than enough of this to redissolve the aurous iodide precipitated at first. A clear solution of starch is then added, and the blue colour produced by it is just removed by thiosulphate. The standard iodine is then added until the liquid assumes a faint rose colour, and the amount of gold is obtained. Of course the gold value of the standard solutions must be ascertained by experiment upon a pure gold solution of known strength. For very small quantities of gold $^N/_{1000}$ solutions of iodine and thiosulphate may be used with good effect, but in this case a correction of 0·1 c.c. for the iodine must be allowed for volumes not exceeding 30 c.c. of the gold, because that is the amount required to bring out the rose colour in a blank experiment. In the practical use of this process for the determination of metallic gold, the metal can of course be got into solution by chlorine water or aqua regia, but in the removal of the excess of the oxidizer by evaporation it is difficult to prevent the formation of aurous chloride. Gooch and Morley, however, found that by adding ammonia in excess to the solution, boiling gently, acidifying with HCl, and heating if necessary to redissolve the precipitate by ammonia, again treating with ammonia and heating, and once more acidifying, the ammonium chloride so formed acts apparently in producing a clear solution ready for titration.

---

[1] *Z. f. Anorg. Chem.*, 1899, **19**, 63.

[2] *Amer. Jour. Sci.*, October, 1899.

Colorimetric Determination of Gold in Ores.—This method is mentioned in *Rose's Metallurgy of Gold* as being of service.

METHOD OF PROCEDURE: Take 100 gm. of the ore, or less if more than a trace of gold, and heat it in a stoppered bottle for some hours with 10 c.c. of bromine and 100 c.c. of water. Then filter off the liquid, and wash the residue several times with water. Evaporate the filtrate till it no longer smells of bromine. Make it up to 100 c.c. and raise it to boiling. Place 5 to 10 c.c. of a fresh saturated solution of stannous chloride in a beaker and rapidly pour upon it the boiling extract. A precipitate will form and sink to the bottom. If no gold be present the precipitate has a slight bluish tint. Gold causes it to be purplish red to blackish purple, according to the quantity present. The gold is determined by taking small quantities of standard gold solution, making up to 100 c.c., boiling and pouring into stannous chloride, exactly as was done with the ore extract. In this way the gold can be approximately determined. The gold present should be between 0·0001 and 0·00002 gm. If there be more than 0·0001 gm. a more dilute extract of ore should be prepared. If less than 0·00002 gm. be present a larger quantity of ore should be used.

Determination of Gold in dilute Cyanide Solutions.—J. Moir[1] gives the following rapid method: 100 c.c. of the solution are boiled for 2 minutes with about 1 gm. of sodium peroxide, to destroy cyanides. Next, two drops of 10 per cent lead acetate solution are added, and about 0·2 gm. of aluminium powder is stirred in. Metallic lead is thus precipitated, and the gold is also extracted by the galvanic action. The whole is filtered when the aluminium has dissolved (the filtrate being free from cyanide as well as gold). The black precipitate is dissolved in 10 c.c. of boiling 60 per cent. aqua regia, and treated carefully with stannous chloride solution until the yellow colour is bleached, whereupon the purple tint (purple of Cassius) develops, and is constant after a minute. It is then compared with a set of artificial standards, after making the liquid up to 15 c.c. in a tube of fixed diameter. The standard tubes are filled with a permanent imitation of "purple of Cassius," made by mixing copper and cobalt salts in the required proportion. They are standardized empirically. The shade is easily visible with solutions carrying 1 part of gold per million, and by looking down the tubes (as in nesslerizing), 2 grains per ton (1 in seven millions) can be detected. Of course, even less than this can be recognized, if more than 100 c.c. of solution be used at the beginning.

IODINE.

I = 126·92.

1. By Distillation.

FREE iodine is of course very readily determined by solution in potassium iodide, and titration with starch, and $^{N}/_{10}$ thiosulphate, as described on p. 134 *et. seq.*

---

[1] *J. S. C. I.*, abstr., **22**, 1257.

Combined iodine in haloid salts, such as the alkali iodides, must be subjected to distillation with hydrochloric acid and some other substance capable of assisting in the liberation of iodine, which is received into a solution of potassium iodide, and then titrated with ${}^N/_{10}$ thiosulphate in the ordinary way. Such a substance presents itself best in the form of ferric oxide, or some of its combinations. If, therefore, hydriodic acid, or, what amounts to the same thing, an alkali iodide, be mixed with an excess of ferric oxide or chloride and distilled in the apparatus shown in fig. 35 or 36, the following reaction occurs:—

$$Fe_2O_3 + 2HI = 2FeO + H_2O + I_2.$$

The best form in which to use the ferric oxide is iron alum.

The iodide and iron alum having been brought into the little flask (fig. 36), sulphuric acid of about 1·3 sp. gr. is added, and the cork carrying the distillation tube inserted. This tube is not carried into the solution of potassium iodide in this special case, but within a short distance of it; and the end must not be drawn out to a fine point, as there represented, but cut off straight. The reason for this arrangement is that it is not a chlorine distillation for the purpose of setting iodine free from the iodide solution, as is usually the case, but an actual distillation of iodine, which would speedily choke up the narrow point of the tube and so prevent the further progress of the operation.

As the distillation goes on, the steam washes the condensed iodine out of the tube into the solution of iodide, which must be present in sufficient quantity to absorb it all. When no more violet vapours are to be seen in the flask, the operation is ended; but to make sure it is well to empty the solution of iodine out of the condensing tube into a beaker, and put in a little fresh iodide solution with starch, then heat the flask again; the slightest traces of iodine may then be detected by the production of the blue colour when cooled. When this takes place the distillation is continued a little while, then both liquids are mixed, and titrated with ${}^N/_{10}$ thiosulphate as usual.

It has been previously stated that the rubber joints to the special apparatus of Fresenius, Bunsen, or Mohr for iodine distillations are objectionable. Topf[1] avoids this by so fitting his apparatus together that, although rubber is used the reagents do not come in contact with it.

Another form of apparatus designed by Stortenbeker[2] is shown in fig. 40, in which rubber joints are entirely dispensed with, and glass connections alone used. The connection between the distilling tube and the absorbing apparatus is a water joint, the tube resting in a socket kept wet with water, the chloride of calcium tube is filled with glass beads, moistened with concentrated solution of potassium iodide, and the connection with the absorbing apparatus is ground in like an ordinary stopper. The absorbing bulbs are immersed in water to the middle of the bulbs, and the immersed portion partially filled with iodide solution.

Ferric chloride may be used instead of the iron alum, but it must be free from nitric acid or active chlorine (best prepared from dry Fe_2O_3 and HCl).

The iodides of silver, mercury, and copper cannot be accurately analysed in this way, but must be specially treated. They should be dissolved in the least possible quantity of sodium thiosulphate solution, and precipitated boiling with sodium sulphide, then filtered; the filtrate contains the whole of the iodine free from metal. The filtrate is evaporated to dryness and ignited, then dissolved in water, and distilled with a good excess of ferric salt.[1]

---

[1] *Z. a. C.*, 1887, **26**, 293.

[2] *Ibid.*, 1890, **29**, 278.

2. Mixtures of Iodides, Bromides, and Chlorides.

Donath[2] has shown that iodine may be accurately determined by distillation in the presence of other halogen salts by means of a solution containing about 2 to 3 per cent. of chromic acid free from sulphuric acid.

In the case of a mixture of iodides and chlorides the action is perfectly regular, and the whole of the iodine may be received into potassium iodide without any interference from the chlorine.

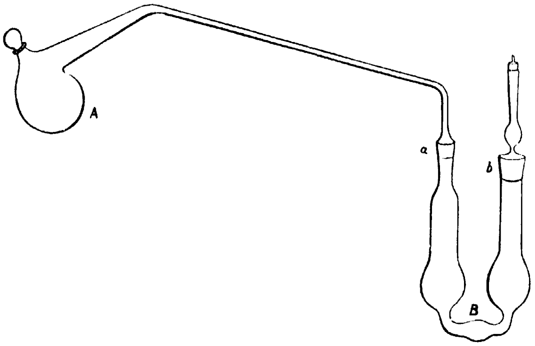

FIG. 40.

In the case of bromides being present, the chromic solution must be rather more dilute, and the distillation must not be continued for more than two or three minutes after ebullition has commenced, otherwise a small amount of bromide is decomposed.

The reaction in the case of potassium iodide may be expressed thus:—

$$6KI + 8CrO_3 = 3I_2 + Cr_2O_3 + 3K_2Cr_2O_7.$$

The distillation may be made in Mohr's apparatus (fig. 36), using about 50 c.c. of chromic solution for about 0·3 gm. I.

The titration is made with thiosulphate in the usual way.

A much less troublesome method of determining iodine in the presence of bromides or chlorides has been worked out by Cook,[3] and depends on the fact that hydrogen peroxide liberates iodine completely from an alkali base in the presence of excess of acetic acid, while neither bromine nor chlorine is affected.

---

[1] Mensel, *Z. a. C.*, 1873, **12**, 137.

[2] *Z. a. C.*, 1880, **19**, 19.

[3] *J. C. S.*, 1885, 471.

Hydrogen peroxide alone will only partially liberate iodine from potassium iodide, but with excess of a weak organic acid to combine with the alkali hydroxide, the liberation is complete. Strong mineral acids must not be used, as bromine and chlorine, if present, would then be set free also.

METHOD OF PROCEDURE: The solution is strongly acidified with acetic acid, and sufficient hydrogen peroxide added to liberate the iodine (5 c.c. will suffice for 1 gm. KI). The mixture is allowed to stand from half an hour to an hour; the whole of the iodine separates, some being in the solid state if the quantity is considerable. Chloroform is now added in sufficient volume to dissolve the iodine, the solution siphoned off, and the globule repeatedly washed with small quantities of water to remove excess of peroxide, then titrated with thiosulphate, with or without starch, in the usual way. If the peroxide is not completely removed by washing, it will decompose the sodium iodide produced in the titration, and so liberate traces of iodine.

The results obtained by Cook in mixtures of bromides, iodides, and chlorides showed about 99 per cent. of the iodine present.

Gooch and Browning[1] publish a method of determining iodine in halogen salts of the alkalies which gives excellent results, and which is based on the fact that arsenic acid in strongly acid solution liberates iodine, becoming itself reduced to arsenious acid, according to the equation

$$H_3AsO_4 + 2HI = H_3AsO_3 + H_2O + I_2.$$

A series of very careful experiments are detailed in the original paper, the outcome of the whole being summarized in the following process:—

METHOD OF PROCEDURE: The substance (which should not contain of chloride more than an amount corresponding to 0·5 gm. of sodium chloride, nor of bromide more than corresponds to 0·5 gm. of potassium bromide, nor of iodide much more than the equivalent of 0·5 gm. of potassium iodide) is dissolved in water in a conical beaker of 300 c.c. capacity, and to the solution are added 2 gm. of potassium binarsenate dissolved in water, 20 c.c. of a mixture of sulphuric acid and water in equal volumes, and enough water to increase the total volume to 100 c.c. or a little more. A platinum spiral is introduced, a trap made of a straight two-bulb drying tube, cut off short, is hung with the larger end downward in the neck of the flask, and the liquid is boiled until the level reaches a mark put upon the flask to indicate a volume of 35 c.c. Great care should be taken not to press the concentration beyond this point on account of the double danger of losing arsenious chloride and setting up reduction of the arsenate by the bromide. On the other hand, though 35 c.c. is the ideal volume to be attained, failure to concentrate below 40 c.c. introduces no appreciable error. The liquid remaining is cooled and nearly neutralized by sodium hydrate (ammonia is not equally good), neutralization is completed by potassium bicarbonate, an excess of 20 c c. of the saturated solution of the latter is added, and the arsenious oxide in solution is titrated by standard iodine in the presence of starch.

With ordinary care the method is rapid, reliable, and easily executed, and the error is small. In analyses requiring extreme accuracy, all but accidental errors may be eliminated from the results by applying the following corrections. These corrections are based on a long series of experiments, which cannot well be given here, but the results may be stated shortly as follows:—

---

[1] *Amer. Jour. Science*, 39, March, 1890, also *C. N.*, 1890, 61, 279.

When no chloride or bromide is present the iodine may be determined with a mean error of 0·2 mgm. in 0·5 gm. or so of the alkali iodide. When sodium chloride is present, there is a slight deficiency in iodine which is proportional to the amount of iodide decomposed. For about 0·56 gm. of potassium iodide and 0·5 gm. of sodium chloride the deficiency in iodine amounted to 0·0011 gm. When the iodide is decreased, say to one-tenth or less, the deficiency falls to 0·0002 gm. The presence of potassium bromide liberates traces of bromine, and consequently increases the AsO_3, and gives apparent excess of iodine, the mean error being 0·0008 gm. for 0·5 gm. of bromide.

The simultaneous action of the chloride and bromide tends of course to neutralize the error due to each. Thus, in a mixture weighing about 1·5 gm. and consisting of sodium chloride, potassium bromide, and potassium iodide in equal parts, the mean error amounts to − 0·0003 gm. The largest error in the series is + 0·0016 gm., when the bromide was at its maximum, and no chloride was present; and the next largest was − 0·0013 gm., when the chloride was at its maximum and no bromide was present.

From a series of experiments detailed in the original paper it was deduced that the amount of iodine to be added, in each case, may be obtained by multiplying the product of the weights in grams of sodium chloride and potassium iodide by the constant 0·004; and the amount to be subtracted, by multiplying the weight in grams of potassium bromide by 0·0016; but in order to make use of these corrections the approximate amounts of these salts present must be known.

For the determination of iodides and bromides in the presence of chlorides, see an elaborate paper by L. W. Winkler[1] (1915).

3. Titration with $^N/_{10}$ Silver Solution and Thiocyanate.

The thiocyanate and silver solutions are described on p. 150 *et seq.*

The iodide is dissolved in 300 or 400 times its weight of water in a well-stoppered flask, and $^N/_{10}$ silver delivered in from the burette with constant shaking until the precipitate coagulates, showing that silver is in excess. Ferric indicator and nitric acid are then added in proper proportion, and the excess of silver determined by thiocyanate as described on p. 150.

4. Oxidation of combined Iodine by Chlorine (Golfier Besseyre, and Dupré).

This wonderfully sharp method of determining iodine depends upon its conversion into iodic acid by free chlorine. When a solution of potassium iodide is treated with successive quantities of chlorine water, iodine is liberated at first, then chloride of iodine (ICl) formed. If starch, chloroform, benzole, or bisulphide of carbon be added, the first will be turned blue, while any of the others will be coloured intense violet. A further addition of chlorine, in sufficient quantity, produces pentachloride of iodine (ICl_5), or rather, as water is present, iodic acid (IO_3H). No coloration of the above substances is produced by these compounds, and the accuracy with which the reaction takes place has been made use of by Golfier Besseyre, and Dupré, independently of each other, for the purpose of determining iodine. The former suggested the use of starch; the latter chloroform or benzole, with very dilute chlorine water. Dupré's method is preferable on many accounts.

---

[1] *Z. angew. C.*, 1915, **28**, 477 and 494; *J. S. C. I.*, 1916, **35**, 305.

Example: 30 c.c. of weak chlorine water were put into a beaker with potassium iodide and starch, and then titrated with $^N/_{100}$ thiosulphate, of which 17 c.c. were required.

10 c.c. of solution of potassium iodide containing 0·010 gm. of iodine were put into a stoppered bottle, chloroform added, and the same chlorine water as above delivered in from the burette, with constant shaking, until the red colour of the chloroform had disappeared: the quantity used was 85·8 c.c. The excess of chlorine was then ascertained by adding sodium bicarbonate, potassium iodide, and starch. A slight blue colour was produced; this was removed by $^N/_{100}$ thiosulphate, of which 1·2 c.c. was used. Now, as 30 c.c. of the chlorine solution required 17 c.c., the 85·8 c.c. required 48·6 c.c. of thiosulphate. From this, however, must be deducted the 1·2 c.c. in excess, leaving 47·4 c.c. $^N/_{100}$ = 4·74 c.c. of $^N/_{10}$ solution, which multiplied by 0·00211, the one sixth of $\frac{1}{10000}$ eq. (1 eq. of iodic acid liberating 6 eq. iodine), gave 0·0100 gm. iodine.

Mohr suggests a modification of this method which dispenses with the use of chloroform or other similar agent.

The weighed iodine compound is brought into a stoppered flask, and chlorine water delivered from a large burette until all yellow colour has disappeared. A drop of the mixture brought in contact with a drop of starch must produce no blue colour; sodium bicarbonate is then added till the mixture is neutral or slightly alkaline, together with potassium iodide and starch; the blue colour is then removed by $^N/_{10}$ thiosulphate. The strength of the chlorine water being known, the calculation presents no difficulty.

Mohr obtained by this means 1·0101 gm. iodine, instead of 1·01 gm.

5. Oxidation by Permanganate (Reinige).[1]

This process for determining iodine in presence of bromides and chlorides gives satisfactory results.

When potassium iodide and permanganate are mixed, the rose colour of the latter disappears, a brown precipitate of manganic peroxide results, and potassium hydroxide with potassium iodide remains in solution. 1 eq. I (= 126·92) reacts with 1 eq. $K_2Mn_2O_8$ (= 316·06), thus—

$$KI + K_2Mn_2O_8 + H_2O = KIO_3 + 2KOH + 2MnO_2.$$

Heat accelerates the reaction, and it is advisable, especially with weak solutions, to add a small quantity of potassium carbonate to increase the alkalinity. No organic matter must be present.

---

[1] *Cf.* L. W. Winkler, *Z. angew. C.*, 1915, **28**, 477 and 494; *J. S. C. I.*, 1916, **35**, 305.

The permanganate and thiosulphate solutions required in the process may conveniently be of $^N/_{10}$ strength, but their reaction upon each other must be definitely fixed by experiment as follows: 2 c.c. of permanganate solution are freely diluted with water, a few drops of sodium carbonate added, and the thiosulphate added in very small portions until the rose colour is just discharged. The slight turbidity produced by the precipitation of hydrated manganic oxide need not interfere with the observation of the exact point.

Method of Procedure: The iodine compound being dissolved in water, and always existing only in combination with alkali or alkaline earthy bases, is heated to gentle boiling, rendered alkaline with sodium or potassium carbonate, and permanganate added till in distinct excess, best known by removing the liquid from the source of heat for a minute, when the precipitate will subside, leaving the upper liquid rose-coloured; the whole may then be poured into a 500-c.c. flask, cooled, diluted to the mark, and 100 c.c. taken out for titration with thiosulphate. The amount so used, being multiplied by 5, will give the proportion required for the whole liquid, whence can be calculated the amount of iodine. To prove the accuracy of the process in a mixture of iodides, bromides, and chlorides, with excess of alkali, the following experiment was made. 7 gm. commercial potassium bromide, the same quantity of sodium chloride, with 1 gm. each of potassium hydrate and carbonate, were dissolved in a convenient quantity of water, and heated to boiling; permanganate was then added cautiously to destroy the traces of iodine and other impurities affecting the permanganate so long as decolorization took place; the slightest excess showed a green colour (manganate). To the mixture was then added 0·1246 gm. pure iodine, and the titration continued as described. the amount found was 0·125 gm. I.

With systematic solutions of permanganate and thiosulphate the calculation is as follows:—

1 c.c. $^N/_{10}$ solution = 0·012692 gm. I.

6. By Nitrous Acid and Carbon Disulphide (Fresenius).

This process requires the following standard solutions:—

(*a*) Potassium iodide, about 5 gm. per litre.

(*b*) Sodium thiosulphate, $\frac{1}{20}$ normal, 12·4 gm. per litre, or thereabouts.

(*c*) Nitrous acid, prepared by passing the gas into tolerably strong sulphuric acid until saturated.

(*d*) Pure carbon disulphide.

(*e*) Solution of sodium bicarbonate, made by dissolving 5 gm. of the salt in 1 litre of water, and adding 1 c.c. of hydrochloric acid.

Method of Procedure: The strength of the sodium thiosulphate in relation to iodine is first ascertained by measuring 50 c.c. of the iodide solution into a 500 c.c. stoppered flask, then about 150 c.c. water, 20 c.c. carbon disulphide, then dilute sulphuric acid, and lastly, 10 drops of the nitrous solution. The stopper is then replaced, and the whole well shaken, set aside to allow the carbon disulphide to settle, and the supernatant liquid poured into another clean flask. The carbon disulphide is then treated three or four times successively with water in the same way till the free acid is mostly removed, the washings being all mixed in one flask; 10 c.c. of disulphide are then added to the washings, well shaken, and if at all coloured the same process of washing is carried on. Finally, the two quantities of disulphide are brought upon a moistened filter, washed till free from acid, a hole made in the filter, and the disulphide which now contains all the iodine in solution allowed to run into a clean small flask, 30 c.c. of the sodium bicarbonate solution added, then brought under the thiosulphate burette, and the solution allowed to flow into the mixture while shaking until the violet colour is entirely discharged. The quantity so used represents the weight of iodine contained in 50 c.c. of the standard potassium iodide, and may be used on that basis to ascertain any unknown weight contained in a similar solution.

When very small quantities of iodine are to be titrated, weaker solutions and smaller vessels may be used.

This process is especially useful in determining small amounts of iodine in the presence of chlorine and bromine, as in mineral waters.

7. By N/10 Silver Solution and Starch Iodide (Pisani).

The details of this process are given under the head of silver assay and are of course simply a reversal of the method there given. This method is exceedingly serviceable for determining small quantities of combined iodine in the presence of chlorides and bromides, inasmuch as the silver solution does not react upon these bodies until the blue colour is destroyed.

8. Determination by Potassium Iodate. See p. 138.
Determination of Iodate. See p. 139.

IRON.

Fe = 55·84.

Factors.

1 c.c. N/10 permanganate, dichromate, or thiosulphate	= 0·005584 Fe
" " "	= 0·007184 FeO
" " "	= 0·007984 Fe_2O_3.

1. Determination of Iron in the Ferrous State.

For this purpose standard solutions of potassium dichromate and potassium permanganate are used.

(1) Potassium Dichromate Method (Penny).

This is the method most generally used and is fully described on p. 132. A decinormal solution of the salt may be employed, but more generally a solution is used (4·390 gm. per litre: 1 c.c. = 0·005 gm. Fe) such that by taking 0·5 gm. of the iron ore the number of c.c. required gives percentage of iron direct. The dichromate solution is standardized with iron wire (99·8 per cent. pure) in one of the following ways:—

(*a*) A known weight of the wire (0·2 – 0·3 gm.) is dropped into a flask fitted with a rubber stopper carrying a Bunsen's valve,[1] and water and a few centigrams of sodium bicarbonate added. Hydrochloric acid (about 15 c.c.) is then added and the rubber stopper as above inserted. The flask is heated till complete solution has taken place, when the stopper is at once removed, rinsed into a basin, the contents of the flask being added and the flask well rinsed out. The titration is then immediately proceeded with.

(*b*) Put into a 220 c.c. flask 25 c.c. of water and heat on a hot plate till boiling. Then drop in the weighed portion (about 0·25 gm.) of iron wire and immediately add 15 c.c. of strong HCl and cover the flask with a glass marble. In 4 to 6 minutes the wire will have dissolved to a perfectly colourless solution, which should then be rinsed out into a basin and the titration with dichromate at once proceeded with.

Another method now much used is to standardize by means of ferric oxide or an iron ore of known iron content: this is dissolved, reduced, and then titrated. The best plan is to stock a quantity of some pure iron ore and to determine the iron content gravimetrically. For each standardization 5 gm. of the ore are dissolved, made up to 200 c.c., and 20 c.c. (= 0·5 gm. of ore) titrated. Magnetic ore is the best for the purpose, as it is not hygroscopic; red hæmatite has a tendency to take up moisture when powdered. Ferric oxide of great purity may be prepared by a somewhat lengthy process from iron, free from cobalt and practically free from phosphorus For full details see L. Brandt, *Chem. Zeit.*, 1916, **40**, 605 *et seq.* (also *J. S. C. I.*, 1916, **35**, 945).

Ferrous ammonium sulphate (p. 129) is a very convenient material for adjusting standard solutions, but it must be most carefully made from pure materials, dried perfectly in the granular form, and kept from the light in small dry bottles, well closed.

(ii) Determination by $^{N}/_{10}$ Permanganate.

This is best carried out in solutions containing no acid other than sulphuric. Where, as is often the case, an iron ore cannot be dissolved in sulphuric acid it is dissolved in HCl and the solution evaporated with sulphuric acid. Carbonaceous ores, bog ores, etc., must be previously freed from organic matters by roasting. 0·5 – 0·1 gm. of the ore is got into solution in a flask, and the iron reduced to the ferrous condition by means of a piece of zinc (free from iron and carbon), the flask being heated on a hot plate and kept covered with a glass marble. When the solution has become colourless or pale green and all the zinc has been dissolved, the solution is cooled, rinsed into a beaker, diluted largely with water that has been boiled and cooled, and titration with permanganate at once proceeded with. When permanganate is run into a solution containing much free HCl, chlorine may be set free, thus:—

$$KMnO_4 + 8HCl = KCl + MnCl_2 + 5Cl + 4H_2O.$$

With a small excess of free acid, a very dilute solution, and low temperature, the titration may, however, be carried out without danger from this secondary reaction, and, in any case, the formation of chlorine is indicated by the smell.

---

[1] A Bunsen's valve fitting consists of a piece of glass tubing carrying a short length of rubber tubing, which is closed at the upper end by a piece of glass rod The rubber tube has a vertical slit, forming the valve, which allows gas or vapour to pass out, but closes by atmospheric pressure when the evolution ceases.

(For Standardization of Permanganate see p. 128).

It should be borne in mind that ferrous compounds are much more stable in sulphuric than in hydrochloric acid solution, and whenever possible sulphuric acid should be used as the solvent. When hydrochloric acid must be used, and permanganate is employed, some manganous or ammonium sulphate should be added unless the solution is very dilute.

Friend[1] finds that accuracy is attained, provided that the manganous sulphate present is not less than 2 gm. in 200 c.c., if (1) the titration is performed slowly with constant shaking, (2) the concentration of the HCl does not exceed $^{N}/_{4}$.

Jones and Jeffrey[2] recommend a modified Zimmermann-Reinhardt process of titration in which the following reagents are employed:—

Reinhardt's Manganese Solution: Dissolve 66⅔ gm. of cryst. manganese sulphate in about 330 c.c. of water in a litre flask, and add to it a cooled mixture of 133 c.c. of concentrated sulphuric acid and 200 c.c. of water, then add 333⅓ c.c. of phosphoric acid (sp. gr. 1·3), and make up to the mark with water.

Mercuric chloride: A cold, saturated solution. Hydrochloric acid: Acid of sp. gr. 1·1. The slight oxidizing power sometimes possessed by the manganese solution, when freshly prepared, may be easily determined and allowed for if necessary; but it has been found that this oxidizing effect is unmeasurable when the solution is a week old. In the presence of hydrochloric acid, permanganate titrations give results which are a little too high, even when the manganese solution is employed; the authors find that the small error so introduced is a constant one, independent of the amount present, and therefore easily allowed for. The titration is carried out as follows:—

The iron solution (in hydrochloric acid of 1·1 sp. gr.) is reduced with the smallest possible excess of stannous chloride, and 10 c.c. of mercuric chloride are added to the cold solution, the mixture being then allowed to stand for 10 minutes to ensure the complete conversion of the stannous salt to the stannic condition, no appreciable oxidation of the reduced iron occurring in the meantime. A quantity of water, which may vary between 400 and 1000 c.c. without appreciable effect on the titration, is then mixed, in a capacious bowl, with a volume of the manganese solution equal to that of the hydrochloric acid present in the assay, and the mixture tinted with permanganate, of which one drop should suffice. The ferrous solution is then transferred to the bowl, together with the rinsings of its containing vessel, and the permanganate added, drop by drop, with constant stirring, until the end point is reached. 0·1 c.c. is then deducted from the burette-reading, and the amount of iron present is calculated by reference to the known titre of the permanganate, as determined by titration against a ferrous solution free from hydrochloric acid.

---

[1] *Chem. Soc. Trans.*, 1909, **95**, 1228.

[2] *Analyst*, 1909, **34**, 306. See also note, p. 130.

G. J. **Hough**[1] claims that the use of phosphoric acid alone in iron solutions to be titrated by potassium permanganate in the presence of hydrochloric acid works perfectly and gives very accurate results. Certain conditions must be observed, i.e. not more than 5 or 10 c.c. of concentrated hydrochloric acid must be present, using 5 c.c. of syrupy phosphoric acid (sp. gr. 1·7), titrating in a cold solution of about 300 c.c. volume, and avoiding reduction by stannous chloride.

2. Reduction of Ferric Compounds to the Ferrous State.

This may be accomplished by metallic zinc or magnesium, for use with permanganate, or by stannous chloride or an alkali sulphite for dichromate solution. The magnesium method is elegant and rapid, but costly. In the case of zinc being used, the metal must either be free from iron or, if it contain any, the exact quantity must be known and allowed for; and further, the pieces of zinc used must be entirely dissolved before the solution is titrated. The solution to be reduced by zinc should not contain more than 0·15 gm. Fe per 250 c.c., and for this quantity about 10 gm. of Zn and 25 c.c. H_2SO_4 are advisable; when the zinc is all dissolved, the whole should be boiled with exclusion of air, then cooled rapidly before titration with the permanganate. The excellent method of reduction by means of stannous chloride solution is fully described on p. 133.

Reduction by Sodium or Ammonium Sulphite.—If sodium sulphite be used, the solution of iron must not be too acid and should be dilute, say a volume of half a litre for ½ gm. of Fe. The sulphite is added and the flask gently heated till the liquid is colourless. It is then boiled briskly till all SO_2 is dissipated; when cooled it is ready for titration with dichromate. In the case of ores containing titanium it is preferable to avoid the use of zinc for reduction, as it also reduces the titanium more or less; alkali sulphite does not.

The procedure with ammonium bisulphite is as follows:—[2] To the acid solution of the ore or metal, diluted and filtered, ammonia is added until a faint precipitate of ferric hydroxide is produced. This is re-dissolved with a few drops of HCl, and some strong solution of bisulphite added, in the proportion of about 1 c.c. for each 0·1 gm. of ore, or 0·05 gm. Fe. The mixture is well stirred, boiling water added, then acidified with dilute sulphuric acid, and boiled for half an hour: it is then ready for titration.

D. J. **Carnegie**[3] points out the value of zinc dust for the rapid reduction of ferric solutions, and suggests the following method of carrying it out.

The bottom of a dry and narrow beaker is covered with zinc dust sifted through muslin. A known volume of ferric solution, previously nearly neutralized with ammonia, is placed in the beaker and shaken with the zinc dust; then a known volume of dilute sulphuric acid is added and shaken for a few moments. The reduction is much more rapid in neutral than in acid solutions, but of course acid in this case must be present in excess to keep the iron in solution. **Carnegie** withdraws a portion of the reduced solution from the undissolved zinc by help of a filter, such as **Beale**'s, and, as measured volumes have been used, an aliquot part taken with a pipette may be at once titrated, and the amount of iron found.[1]

---

[1] *J. A. C. S.*, 1910, **32**, 539.

[2] **Austen**, *C. N.*, 1882, **46**, 287.

[3] *J. C. S.*, 1888, **53**, 468.

Clemens Jones[2] in a paper read before the American Institute Mining of Engineers, adopts the plan suggested by Carnegie, and has designed a special apparatus for filtering the ferric solution through a column of zinc dust. This arrangement gives complete reduction in a very short period of time, and is serviceable where a large number of titrations have to be carried on.

DETERMINATION OF IRON IN THE FERRIC STATE.

1. Direct Titration of Iron by Stannous Chloride (see p. 133).

Determination of Iron in Pharmaceutical Syrups.—(Richmond and Ison).[3] To 5 or 10 c.c. of the syrup a few drops of strong hydrochloric acid are added, and $^N/_{10}$ permanganate solution run in until a transitory purple coloration is produced throughout the solution. Coloured syrups are decolorized and the iron present is entirely in the ferric state. An equal volume of strong hydrochloric acid is added, then a little sodium bicarbonate to give an atmosphere of CO_2, and $^N/_{10}$ stannous chloride solution added, a drop at a time, until a drop of the mixture gives a blue coloration with ferricyanide. The titration with stannous chloride is then started, and continued until a drop of the mixture no longer gives a colour with thiocyanate solution.

1 c.c. $^N/_{10}$ stannous chloride solution = 0·005584 gm. Fe.

2. Direct Titration of Iron by Titanous Chloride.

Titanous chloride ($TiCl_3$)[4] which was employed in the first place as a reducing agent for the determination of ferric iron, has lately received much wider application in the domain of volumetric analysis, it being now successfully used for the quantitative determination of nitro-compounds, the azo-dyes and dyestuffs, etc.[5]

The readily oxidizable solution of titanous chloride is prepared and stored as follows:—

50 c.c. commercial titanous chloride (20 per cent. solution) and 100 c.c. conc. HCl are boiled together in a small flask for about a minute, the mixture is cooled, made up to about 2½ litres, thoroughly mixed by shaking, and the storage bottle A (see fig. 41) filled up to the neck with the solution.

---

[1] Commercial zinc dust is probably a by-product in zinc manufacture, and cannot therefore be obtained pure. Samples examined by myself, and apparently by others also, do not, however, contain much iron, but a good deal of zinc oxide, with traces of cadmium and lead. Carnegie states that the oxide may be removed by repeatedly digesting with weak acid, or better still, by treatment with ammonium chloride and ammonia, the well-washed dust being finally dried on porous tiles in a vacuum. I find that by washing once with strong alcohol after the water and finally with ether, the dust may be rapidly dried in good condition, and when a quantity of such purified dust is obtained, the amount of iron in it may easily be determined once for all, and allowed for in titration. Good zinc dust is undoubtedly a valuable reagent in a laboratory for other purposes besides iron titrations.

[2] *C. N.*, 1889, **60**, 93.

[3] *Analyst*, 1920, **45**, 258.

[4] Three chlorides of titanium are known, $TiCl_2$, $TiCl_3$, and $TiCl_4$. Of these $TiCl_2$ is the true titanous chloride.

[5] See Knecht and Hibbert, *New Reduction Methods in Volumetric Analysis*, 1910.

The mode of connection of this bottle with the burette (B) will readily be seen by the fig. 41. Rubber stoppers are used and at D_1 and D_2 are valves constructed of glass rod and rubber tubing as described on p. 11. C is a hydrogen generator consisting of a glass cylinder half filled with dilute HCl (1 : 1) into which dips an inner tube contracted at the bottom to a narrow aperture and filled with ordinary granulated zinc. The hydrogen generated when D_2 is opened passes into the storage bottle and burette. By opening the valve D_1 the titanous chloride flows into the burette and rises into the tube above it, then by opening D_2 the solution is entirely run out and the hydrogen allowed to escape for some minutes. The burette can now be filled up to the zero mark and the apparatus is ready for use.

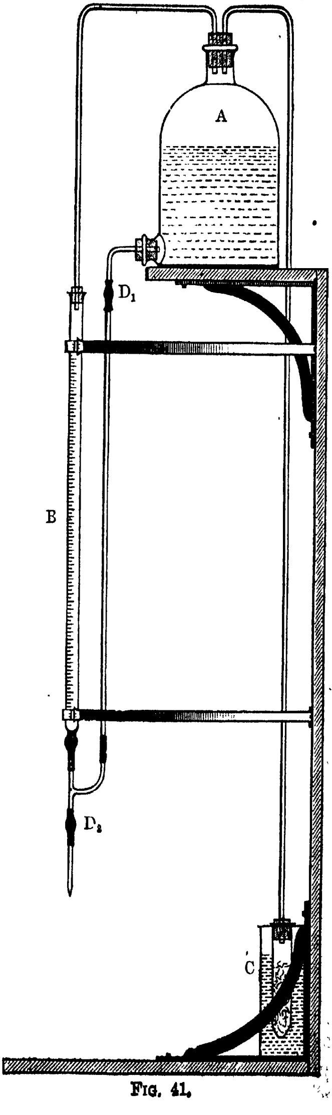

FIG. 41.

Standardization of the Solution.—Dissolve 3·511 gm. of the purest ferrous ammonium sulphate in water, add about 100 c.c. 5 N . H_2SO_4, and make up the solution to 250 c.c. in a measuring flask. Pipette 25 c.c. (= 0·05 gm. Fe) of the well mixed solution into a flask and carefully oxidize with permanganate of about $^N/_{50}$ strength until a faint pink tinge is obtained. Then add a **large excess**[1] of potassium sulphocyanate and run in the titanous chloride from the burette until the red colour, due to ferric sulphocyanate, has entirely disappeared. Suppose, for example, that 25 c.c. of the iron solution, after oxidation, require 26·3 c.c. titanous chloride to reduce it, then

---

[1] A large excess renders the end-reaction much sharper.

$$1 \text{ c.c. } TiCl_3 = 0{\cdot}0019 \text{ gm. Fe.}$$

Solutions of ferric iron, to which an excess of potassium sulphocyanate is added as indicator, can be titrated directly with the titanous solution. It is immaterial whether the iron is present in sulphuric or hydrochloric acid solution, but the presence of some mineral acid is essential, as otherwise the indicator is not sensitive. Ferrous iron must first be oxidized to the ferric state. This is generally done as follows :—

To a measured volume of the solution add ammonia and hydrogen peroxide, and remove the excess of oxygen by boiling the liquid for 5 to 10 minutes. Then add HCl in quantity more than sufficient to dissolve the ferric hydrate ; or :

To the ferrous solution add a crystal of $KClO_3$ and some HCl, boil down to a small bulk, add water or HCl, again evaporate down, and when the excess of chlorine has thus been removed the solution is ready for titration.

The reaction which takes place is

$$FeCl_3 + TiCl_3 = FeCl_2 + TiCl_4.$$

3. Titration by Sodium Thiosulphate.

Scherer first suggested the direct titration of iron with thiosulphate, which latter was added to a solution of ferric chloride until no further violet colour was produced. This was found by many to be inexact ; but Kremer[1] has made a series of practical experiments, the result of which is that the following modified method can be recommended.

The reaction which takes place is such as to produce ferrous chloride, sodium tetrathionate, and chloride. $2Na_2S_2O_3 + Fe_2Cl_6 + 2HCl = H_2S_4O_6 + 4NaCl + 2FeCl_2$. The thiosulphate, which may conveniently be of $^N/_{10}$ strength, is added in excess, and the excess determined by iodine and starch.

METHOD OF PROCEDURE : The iron solution, containing not more than 1 per cent. of metal, which must exist in the ferric state without any excess of oxidizing material (best obtained by adding excess of hydrogen peroxide, then boiling till the excess is expelled), is moderately acidified with hydrochloric acid, sodium acetate added till the mixture is red, then dilute hydrochloric acid until the red colour disappears ; then diluted till the iron amounts to ½ or ¼ per cent., and $^N/_{10}$ thiosulphate added in excess, best known by throwing in a particle of potassium sulphocyanide after the violet colour produced has disappeared ; if any red colour appears, more thiosulphate must be added. Starch and $^N/_{10}$ iodine are then used to ascertain the excess. A mean of several experiments gave 100·06 Fe, instead of 100.

J. T. Norton[2] has carefully experimented on this method and found that it needs careful management to ensure accurate results. The volume of dilution and amount of acid must be carefully regulated, so also must the amount of thiosulphate used in excess. There should always be at least 15 c.c. of thiosulphate in excess with 0·1 gm. of ferric oxide and 1 c.c. of strong hydrochloric acid in not less than 400 or 500 c.c. of freshly boiled water used for dilution. The time occupied in reduction should be as short as possible.

---

[1] *Journ. f. Pract. Chem.*, **84**, 339.

[2] *J. A. C. S.*, 1899, **21**, 25.

METHOD OF PROCEDURE: In treating ferric oxide, the following method is recommended: Dissolve an amount not exceeding 0·2 gm. of the oxide in 2 c.c. of hydrochloric acid, evaporate to a pasty mass, dilute to about 800 c.c. with freshly-boiled water, add a drop of potassium sulphocyanide, and into this solution run 50 c.c. of $^{N}/_{10}$ sodium thiosulphate; allow the liquid to stand until perfectly colourless, and determine the excess of thiosulphate by $^{N}/_{10}$ iodine and starch. For quantities of iron oxide up to 0·2 gm. this process is quick and most accurate; when care is taken to preserve the relations of acidity and dilution, twice the amount of ferric oxide mentioned above may be handled.

The accuracy of the process is not interfered with by the presence of salts of the alkalies, strontia, lime, magnesia, alumina, or manganous oxide; neither do salts of nickel, cobalt, or copper, unless their quantity is such as to give colour to the solution.

The process is a rapid one, and with care gives very satisfactory results.

4. Determination with Iodine and Sodium Thiosulphate.

When ferric chloride is digested with potassium iodide in excess, iodine is liberated, which dissolves in the free potassium iodide—

$$FeCl_3 + KI = FeCl_2 + KCl + I.$$

METHOD OF PROCEDURE: The hydrochloric acid solution, which must contain no free chlorine or nitric acid, and all the iron in the ferric state, is nearly neutralized with caustic potash or soda, transferred to a well-stoppered flask, and an excess of strong solution of potassium iodide added; it is then heated to 50° or 60° C. on the water bath, closely stoppered, for about twenty minutes; the flask is then cooled, starch added, and titrated with thiosulphate till the blue colour disappears. This process gives very satisfactory results in the absence of all substances liable to affect the potassium iodide, such as free chlorine or nitric acid, and is particularly serviceable for determining small quantities of iron.

Instead of starch another indicator is suggested by Haswell.[1] To an aliquot portion of the solution of the ferric salt a little cupric sulphate and salicylic acid are added as an indicator, and then from a burette standard thiosulphate solution is run in until the violet coloration is entirely destroyed. The liquid is then titrated back with the solution of the ferric salt, until the colour just reappears.

Joseph[2] has shown that good results may be obtained by the following simplified procedure:—

To the ferric solution, acidified with HCl (the quantity used seems to be of no practical importance), add a few grams of KI, and at once titrate the iodine liberated with $^{N}/_{10}$ thiosulphate. In those frequent cases where the substance *must* be dissolved in HCl and potassium chlorate, on account of the presence of ferrous iron, the liquid is boiled almost to dryness before titration.

---

[1] *Z. f. angew. Chem.* 1902, **15**, 1265.

[2] *J. S. C. I.*, 1910, **29**, 187.

1 c.c. $^N/_{10}$ thiosulphate = 0·005584 gm. Fe.

The solution is standardized either with iodine or with iron alum. Excellent results are recorded.

5. Determination of Iron Colorimetrically.

(i) Thiocyanate Method.

The determination of minute quantities of iron in the presence of large quantities of other metals, more especially in alloys, has been carefully worked out by Andrew Thomson,[1] who claims that the sensitiveness of his method is such that 1 part of iron in 50,000,000 parts of water can be detected and determined. (It is, therefore, more sensitive than any other known colorimetric method, for the Nessler test, which has hitherto been considered the most delicate, allows of the estimation of 1 part of ammonia in but 20,000,000 of water.) The process depends upon the well-known blood-red coloration produced by the action of ferric salts on potassium thiocyanate, and has been found to be almost universally applicable; silver and copper, and in some cases cobalt, being the only common metals that interfere with its action. Thomson records results showing accurate determinations by this method of small amounts of iron in admixture with lead, mercury, cadmium, bismuth, arsenic, tin, antimony, nickel, cobalt, manganese, calcium, aluminium, zinc, strontium, barium, magnesium, sodium, and potassium. The presence of even large quantities of organic matter does not affect the reaction. Mercurous and stannous salts, when present, should be converted into the mercuric and stannic salts, otherwise the colour is destroyed. It is also destroyed by even minute quantities of oxalic acid, though the presence of arsenic and phosphoric acids does not affect it, provided there be plenty of acid present. Although mercuric chloride in a neutral or nearly neutral solution, as is well known, instantly bleaches the red colour produced by thiocyanates with ferric chloride, if 5 c.c. of nitric or hydrochloric acid (1 : 5) be added, the red colour persists even after standing for 15 or 20 minutes.

The following solutions are required :—

1. *Standard Solution of (Ferric) Iron.*—(*a*) Dissolve 0·7022 gm. of ferrous ammonium sulphate in water, add 5 c.c. of dilute sulphuric acid (1 : 5), then run in with caution a dilute solution of potassium permanganate (containing about 2 gm. per litre, and of this solution about 29 c.c. will be required) till a slight pink coloration remains after well stirring; or hydrogen peroxide may be used in place of permanganate, taking care to dissipate the excess by boiling. The solution is then diluted with water to 1 litre :—

1 c.c. = 0·0001 gm. Fe.

(*b*) Dissolve 1·004 gm. of pure iron wire, which has been first cleaned with emery paper and then wiped with a dry cloth, in nitro-hydrochloric acid, precipitate with ammonia, filter, wash, re-dissolve the ferric hydroxide in a little hydrochloric acid, and dilute to 1 litre. Of this 100 c.c. are diluted to 1 litre, of which

---

[1] *J. C. S.*, 1885, 47, 493.

1 c.c. = 0·0001 gm. Fe.

2 c.c. of either of the above solutions, when acidified and mixed with thiocyanate and diluted to 100 c.c. give a convenient colour for comparison.

2. *Potassium Thiocyanate Solution.*—10 gm. of the crystallized salt are dissolved in 250 c.c. of water.

3. *Dilute Hydrochloric or Nitric Acid.*—(1 : 5).

METHOD OF PROCEDURE : Dissolve a weighed portion of the substance in which the amount of iron is to be determined in a suitable acid, and evaporate nearly to dryness to expel excess of acid. After slightly diluting with water, convert the iron into the ferric state by adding a dilute solution of permanganate, and make up the liquid to 1 litre or other suitable volume. Into each of two short 100 c.c. Nessler glasses pour 5 c.c. of the dilute acid (3) and 15 c.c. of the thiocyanate solution (2). Then add to one 2 c.c. of the standard iron solution (1) and to the other a measured quantity of the solution to be tested, using such an amount as to make the depth of colour in the two cylinders approximately equal. The liquids are made up to the mark with water in each case, thoroughly mixed and "nesslerized". Thus, suppose 20 c.c. of a solution containing iron to be taken and made up to 100 c.c. as above, and that 85 c.c. of the latter exactly matched in colour the standard, the amount of iron present in the 20 c.c. of solution taken would be $\frac{100}{85} \times {\cdot}0002 = 0{\cdot}000235$ gm. Fe.

In all cases, the more strongly coloured liquid should be diluted with water to 100 c.c. and well mixed before final comparison.

The above method acts admirably for the determination of small quantities of **iron in water,** for which purpose Carter Bell[1] adopts the following procedure:—

70 c.c. of the water are evaporated to dryness in a platinum dish, and gently ignited to burn off organic matter. 1 c.c. of dilute nitric acid (50 c.c. of strong acid in a litre) is then poured over the residue and evaporated to dryness on the water-bath; the residue is then dissolved in 1 c.c. of 10 per cent. HCl (1 : 4), 5 or 10 c.c. of water added, the solution filtered through a small filter, washed, and transferred to a Nessler glass and either treated as above or by the following method:—

(ii) Ferrocyanide Method.

Solution required.—*Potassium ferrocyanide,* the usual N solution (105·5 gm. per litre).

The procedure is exactly similar to that followed in the thiocyanate method described above. 2 c.c. of the standard iron solution are measured into one cylinder and a measured portion of the dilute iron solution to be tested into another. To each cylinder are then added, first 1 c.c. of concentrated nitric acid (the presence of free acid is essential), then water and 1 c.c. of ferrocyanide, the liquid made up to 100 c.c. with water and well mixed. If the tints of the two liquids are approximately equal, they are allowed to stand for a few minutes to develop the full colour, and then nesslerized. If not, an approximate comparison should be at once made by pouring some of the darker liquid into a measuring cylinder and then, after calculating the approximate amount to be measured out, making up a new solution of nearly the same colour, and nesslerizing after a few minutes' standing.

---

[1] *J. S. C. I.,* 1889, **8**, 175.

This method acts well, but presents no advantages over the thiocyanate method.

IRON ORES, IRON AND STEEL.

THE great desideratum in the analysis of iron ores is to get them into the finest possible state of division, and 10 minutes' hard work with the agate mortar will often save hours of treatment of the material with acids. The operator of experience can generally tell if the ore to be examined will dissolve in acids. Some clay ironstones and brown hæmatites contain organic matters, and they are best first roasted in an open platinum crucible, gradually raising the heat to redness; this course is advisable also when an ore contains pyrites; this latter is easily converted to Fe_2O_3 by roasting. Some ores give a residue in any case by treatment with HCl; this should be separated by filtration and fused with fusion mixture, which will render all the iron in a soluble state. In the analysis of iron ores the total percentage of iron and that existing in both the ferrous and ferric states are usually required. For this purpose 0·5 gm. is taken, ignited gently, if necessary, to destroy organic matters, etc., transferred to a 220 c.c. flask, dissolved in HCl (15 to 20 c.c.), the ferric salt reduced by stannous chloride and the total iron determined by titration with potassium dichromate solution, as fully described on p. 133. To determine the FeO 0·5 or 1 gm. of the ore (according to the amount of FeO present) is put into a 220 c.c. flask and water and about 0·25 gm. of sodium bicarbonate[1] added. The flask is closed with a rubber stopper carrying a Bunsen's valve fitting (see p. 237),—or simply covered with a glass marble—heated to boiling on a hot plate, and about 20 c.c. of strong HCl added, the flask being immediately closed after the addition. Gentle boiling is then continued till nothing but fairly white siliceous residue remains undissolved. The contents of the flask are then transferred to a dish and at once titrated with dichromate. The ferrous iron is thus obtained, and the ferric oxide present is calculated, in the absence of pyrites, from total iron less that in the ferrous state.

Iron ores containing pyrites in any appreciable amount must be roasted in a platinum crucible before being dissolved as above for determination of total iron, and iron so combined must be allowed for before calculating the ferric oxide present.

Ferrous iron may also be determined by means of the following apparatus due to Mohr.

The left-hand flask contains the weighed ore in a finely powdered state, to which tolerably strong hydrochloric acid is added; the other flask contains distilled water only, the tube from the first flask reaching to the bottom of the second. When the ore is ready in the flask, and the tubes fitted, hydrochloric acid is poured in, and a few grains of sodium bicarbonate added to produce an evolution of CO_2. The air of the flask is thus expelled, and as the acid dissolves the ore, the gases evolved drive out in turn the CO_2, which is partly absorbed by the water in the second flask. When the ore is all dissolved, the lamp is removed, and the water immediately rushes out of the second flask into the first, diluting and cooling the solution of ore, so that, in the majority of cases, it is ready for immediate titration. If not sufficiently cool or dilute, a sufficient quantity of boiled and cooled distilled water is added.

---

[1] In the case of calcareous iron ores or spathose ore, which is an impure ferrous carbonate, this will not be required.

Reduction to the ferrous state by means of sodium sulphite, etc, is described on p. 239.

Determination of Iron in Silicates.—Wilbur and Whittlesey[1] give a series of determinations of iron existing in various silicates, either as mixtures of ferric and ferrous salts or of either separately, which appear very satisfactory.

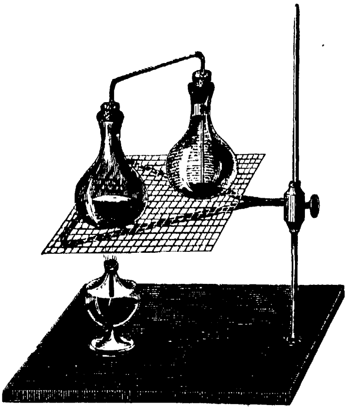

FIG. 42.

The very finely powdered silicate is mixed with rather more than its own weight of powdered fluor-spar or cryolite (free from iron) in a platinum crucible, covered with hydrochloric acid, and heated on the water-bath until the silicate is all dissolved. During the digestion either carbonic acid gas or coal-gas free from H_2S is supplied over the surface of the liquid so as to prevent access of air. When decomposition is complete (the time varying with the nature of the material), the mixture is diluted and titrated with permanganate in the usual way for ferrous oxide; the ferric oxide can then be reduced by zinc and its proportion found.

By Hydrofluoric Acid.—Silicates may also be decomposed by hydrofluoric acid, about 2 gm. being treated with 40 c.c. of the acid (containing about 20 per cent. HF) in a deep platinum crucible. In this case Leeds[2] recommends that the finely powdered silicate be mixed with a suitable quantity of dilute sulphuric acid, and air excluded by CO_2 during the action of the hydrofluoric acid, which should be aided by heat. When decomposition is complete, the crucible and its contents are quickly cooled, diluted with recently boiled water, and the ferrous salt determined with permanganate or dichromate as usual.

---

[1] *C. N.*, 1870, **22**, 2.

[2] *Z. a. C.*, 1877, **16**, 323.

If the hydrofluoric acid has been prepared in leaden vessels, it invariably contains SO_2; in such cases it is necessary to add to it, previous to use, some hydrogen peroxide (avoiding excess) so as to oxidize the SO_2.

The process is a rapid and satisfactory one, yielding much more accurate results than the method of fusion with alkali carbonates or acid potassium sulphate.

Colorimetric Determination of Carbon in Steel.—(Eggertz's process.) This well-known method is not available for steels containing large percentages of chromium, copper and nickel, all of which, especially the first named yield coloured solutions with nitric acid. In such cases the combustion method should be resorted to. When only a moderate percentage of nickel or copper, or a very small percentage of chromium, is present, fairly accurate results may be obtained colorimetrically.

Filings are useless for this process. Drillings should be made with dry tools, quite free from oil, etc., and, if possible, the bar to be sampled should be drilled right through and the whole of the drillings thoroughly mixed.

Reagent required.—Nitric acid of sp. gr. 1·2. Chemically pure acid (free from chlorine) should be used, and 100 c.c. of the acid of sp. gr. 1·42 added to 155 c.c. of distilled water will give a solution of about the right strength, which should be determined by the hydrometer and adjusted if necessary.

METHOD OF PROCEDURE: In all cases steels should be compared with a standard steel of known carbon content, which should be approximately equal to that in the sample to be tested. In cases where the carbon content is entirely unknown a preliminary trial must be made in order to ascertain roughly the amount present. The weight of steel and amount of nitric acid to be taken are then found from the following table.

Carbon per Cent. in Steel.	Carbon per Cent. in Standard Approximately.	Weight of Steel (gm.).	C.c. of HNO_3 (1·2).
1·3—1·7	1·5	0·05	3
1·1—1·3	1·2	0·05	3
0·8—1·1	0·9	0·10	4
0·4—0·8	0·6	0·10	3
0·2—0·4	0·3	0·10	2
0·1—0·2	0·15	0·30[1]	6

The carefully weighed portions of the sample and of the appropriate standard are each put into a marked thin test-tube (6 ins. × ½ in.), which must be scrupulously clean and perfectly dry. The requisite volume of

[1] In this case use a test-tube 6 × 1 ins.

nitric acid is then added to each from a 50 c.c. burette. The tubes are left in the rack for a few minutes, till the first violent evolution of nitrous fumes has ceased. The tubes are next placed in a bath of water kept just boiling on the hot plate, and are occasionally shaken till bubbles of gas are no longer given off and the solutions are clear. This will be from 15 to 30 minutes. The tubes are then well cooled in a vessel of cold water. Comparison is then made in the usual way, in a pair of graduated tubes of colourless glass, using 12 c.c. tubes for all steels containing 0·2 per cent. and upwards of carbon and 20 c.c. tubes for those containing between 0·1 and 0·2 per cent. of carbon. If necessary the solutions must be filtered through a small filter, the test-tube and residue being washed with a fine jet of water till colour-free, and of course made up exactly to 12 or 20 c.c.[1]

Determination of Phosphorus in Iron and Steel.

Pig Iron.—2 gm. of the borings are placed in a 600 c.c. beaker, 20 c.c. of water added, then gradually 16 c.c. of strong nitric acid, the beaker being covered during the process. When violent action has ceased, rinse the cover and sides of the beaker with a small quantity of hot water and evaporate to complete dryness on a hot plate—and bake the residue. Allow to cool, then add 25 c.c. of strong HCl and heat on hot plate till all has dissolved except a black residue of graphitic carbon etc., and evaporate off the excess of acid, the bulk being reduced to about half. Add about 100 c.c. of hot water, filter into a 400 c.c. beaker and wash well. Partially neutralize the hot filtrate with 2½ per cent. ammonia, add 25 c.c. of 50 per cent. ammonium nitrate solution, heat to about 80° and add 30 to 40 c.c. of 10 per cent. ammonium molybdate solution. Allow to stand for about 2 hours on the top of the water-oven, pour off some of the clear liquid and test for complete precipitation by adding about 10 c.c. more molybdate. The precipitate is then filtered off by suction through asbestos in a Gooch crucible, and is washed first with 1 per cent. nitric acid, then with 1 per cent. potassium nitrate solution until free from acid, and then transferred together with the asbestos to a conical flask with a small quantity of water. $^{N}/_{2}$ NaOH is added from a burette in quantity more than sufficient to dissolve the precipitate, the liquid is boiled until all the ammonia has been driven off, cooled and titrated residually with $^{N}/_{2}$ H_2SO_4 and phenolphthalein.

1 c.c. $^{N}/_{2}$ NaOH = 0·000664 gm. phosphorus. See "Notes" below.

Steel.—Dissolve 5 gm. of the borings in 20 c.c. of water and 40 c.c. of strong nitric acid and proceed as with pig iron. The baked residue should be treated with 35 c.c. of strong HCl and rather less ammonium molybdate solution will be required.

Notes.—The above titration is based on the following reaction :—

$$2[(NH_4)_3(MoO_3)_{12}PO_4] + 46\,NaOH + H_2O = 2[(NH_4)_2HPO_4] + (NH_4)_2MoO_4 + 23Na_2MoO_4 + 23\,H_2O$$

from which we find that 1874·142 parts of molybdate precipitate correspond to (23 × 40·008) = 920·184 parts of sodium hydroxide; or taking the precipitate to contain 1·63 per cent. phosphorus, 1 litre of normal soda solution is equal to

---

[1] Arnold and Ibbotson, *Steel Works Analysis*, Third Edition, 1907.

$$\frac{1874{\cdot}142 \times {\cdot}0163}{23} = 1{\cdot}328 \text{ gm. P.}$$

Hence on this basis 1 c.c. of $^N/_2$ NaOH = 0·000664 gm. P. But the true working equivalent is best determined by the method given below.

In place of $^N/_2$ NaOH and $^N/_2$ H_2SO_4 A. A. Blair[1] recommends the use of special standard solutions of alkali and acid prepared as follows:—

Standard Solution of Sodium Hydroxide.—To 100 gm. of pure NaOH add an amount of water just insufficient completely to dissolve it. Pour it into a tall cylinder, close the latter, and allow to settle. 30 c.c. of the clear liquid, which will be practically free from carbonate, are mixed with 2 litres of water.

Standard Nitric Acid.—Mix 20 c.c. of nitric acid (1·42 sp. gr.) with 2 litres of water.

Pipette 10 c.c. of the standard NaOH solution into a small flask, add 40 c.c. of water and 3 drops of phenolphthalein solution, then run in standard nitric acid from a burette until the pink colour just disappears. If the solutions are not of the same strength, dilute the stronger with water till they agree. The standardization is carried out thus. Titrate the ammonium phospho-molybdate obtained from a steel in which the phosphorus has been carefully determined, and divide the percentage of phosphorus by the number of c.c. of the standard solution of sodium hydroxide required to neutralize it. The result is the value of that solution, The solutions may also be so adjusted that 1 c.c. = 0·0002 gm. phosphorus. this result being obtained by calculating the weight of phosphorus to which each c.c. of the solutions is equivalent and diluting to the exact strength required.

Instead of running in the standard NaOH solution from a burette, Blair recommends the addition of the solution by means of a pipette, 10 c.c. being run in at first and further portions of 10 c.c. if necessary, until the precipitate is dissolved, agitating after each addition. The solution is not boiled, but simply diluted to 50 c.c., phenolphthalein added, and the standard nitric acid run in from a burette till the pink colour disappears. The number of c.c. so used is subtracted from the c.c. of NaOH solution taken to dissolve the precipitate, and the phosphorus content then calculated from the remainder.

Determination of Sulphur in Iron and Steel.—J. Thill[2] gives the following method:—

> Method of Procedure: By attacking the metal with hydrochloric acid in the well-known apparatus used for this purpose, the sulphur is liberated as sulphuretted hydrogen. The gas is received in 25 c.c. of a decinormal solution of arsenious acid, to which has been added 50 c.c. of a cold saturated solution of bicarbonate of soda. Care should be taken that the gas is not given off too rapidly.
>
> When the attack is finished, the gas which still fills the apparatus is driven out by means of a current of carbonic acid, and the passage of this current of gas is

---

[1] *The Chemical Analysis of Iron*, Eighth Edition, 1918.

[2] *Z. a. C.*, 1899, **38**, 342.

continued until the hydrochloric acid carried with it has neutralized the alkaline solution, and precipitated almost the whole of the trisulphide of arsenic. This operation takes 8 or 10 minutes.

A few c.c. of hydrochloric acid are added, and the volume made up to 500 c.c. and filtered. The filtrate is collected in a dry beaker, and 100 c.c. are taken, and titrated with $^N/_{10}$ iodine, after adding starch and a sufficient quantity of ammonium carbonate to render the solution alkaline.

From the number of c.c. of iodine used is subtracted the number of c.c. required by 25 c.c. of a decinormal solution of arsenious acid. The difference corresponds to the sulphuretted hydrogen given off. This result, multiplied by 0·0024 gives the amount of sulphur contained in the sample.

At the National Physical Laboratory, Bushy House, Teddington, the volumetric determination of sulphur is carried out thus:—[1]

The steel drillings are dissolved in an evolution flask in hydrochloric acid of 1·10 sp. gr., the operation being aided by heat, although boiling the acid should be avoided. Prior to the commencement of the operation, the evolution flask and entire apparatus are filled with an atmosphere of carbon dioxide, obtained by passing a stream of this gas, derived from a cylinder of liquid carbonic acid, through the entire apparatus. The evolved gases, aided towards the end of the operation by a further stream of CO_2 are bubbled through an absorption flask containing a solution of cadmium acetate strongly acidified with acetic acid (25 gm. pure cadmium acetate and 100 gm. glacial acetic acid per litre). After passing this flask the gases pass through a narrow-bore tube of vitreous silica heated to redness by a Bunsen burner with a flat flame, the gases passing finally through a second cadmium acetate absorption flask and then away to the fume chamber. When the steel has completely dissolved, the contents of the two absorption flasks are mixed and the yellow cadmium sulphide is filtered off; this is a rapid operation since the flask need not be washed carefully,—the operation is merely intended to separate the sulphide from the bulk of the absorption liquid. As soon as this has been done the precipitate is washed from the filter back into the original flask, and there dissolved in 10 c.c. of standard iodine solution,[2] the action being aided by the addition of a small quantity of HCl. The excess of iodine is then titrated by means of sodium thiosulphate and starch. It is to be observed that while this titration can be carried out in the liquid of the absorption flasks without filtration, it has been found that this occasionally leads to discrepancies in the results. Apparently, particularly in the case of high carbon steel, the evolved gases carry into the absorption flask something which is capable of absorbing iodine, but which is not sulphur; this disturbing substance can be eliminated by the filtration described above. A table is given showing the comparative results obtained by this process and by the gravimetric (oxidation) method, the agreement in all cases being exceedingly close.

Note.—From the equation $H_2S + I_2 = 2HI + S$ it follows that

---

[1] Rosenhain, *Iron and Steel Institute Journal*, Vol. I., 1908.

[2] 2 gm. of re-sublimed iodine are dissolved in 50 c.c. of water containing 4 gm. of KI, and diluted to 1 litre.

1 c.c. $^N/_{10}$ iodine = 0·001603 gm. sulphur, or 0·03207 per cent. when 5 gm. are taken.

If to 100 c.c. $^N/_{10}$ iodine solution are added 60·3 c.c. of water, a solution is obtained containing 7·94 gm. iodine per litre, and of this 1 c.c. = 0·001 gm. S.

LEAD.

Pb = 207·2.

THE accurate determination of lead is in most cases better effected by weight than by measure; there are, however, instances in which the latter may be used with advantage. The precipitation as oxalate or carbonate is only of use where the lead exists in the form of a tolerably pure salt or metal.

1. As Oxalate (Hempel).—The lead solution strongly acidified with acetic acid, which must contain no other body precipitable by oxalic acid, is put into a 300 c.c. flask, and a measured quantity of normal oxalic acid added in good excess, the flask filled to the mark with water, shaken, and put aside to settle; 100 c.c. of the clear liquid may then be taken, acidified, with sulphuric acid, and titrated with permanganate for the excess of oxalic acid. The amount so found multiplied by 3, and deducted from that originally added, will give the quantity combined with the lead.

2. Alkalimetric Method (**Mohr**).—The lead is precipitated as carbonate by means of a slight excess of ammonium carbonate, together with free ammonia; the precipitate well washed, and dissolved in a measured excess of normal nitric acid; neutral solution of sodium sulphate is then added to precipitate the lead as sulphate. Without filtering, the excess of nitric acid is then determined by normal alkali, each c.c. combined being equal to 0·10355 gm. of lead.

3. Dichromate Method[1].—1 c.c. $^N/_{10}$ dichromate = ·01036 gm. Pb.

The following process for carbonate ores, pig lead, and specially for red and white leads and litharge, has been worked out by J. H. Wainwright.[2] The necessary solutions are: potassium dichromate, of such strength that 1 c.c. represents about 0·01 gm. of metallic lead, not much more nor less, standardized either upon pure metal, or on white lead which has been accurately analysed for actual lead by weight: silver nitrate solution as outside indicator, not exceeding 2 or 3 per cent. in strength.

METHOD OF PROCEDURE: From 1 to 1·5 gm. of ore, litharge, etc., is dissolved in 10 to 15 c.c. of nitric acid (sp. gr. 1·20), the solution made slightly alkaline with ammonia, and a considerable excess of acetic acid added. It is then boiled, and potassium dichromate solution, in sufficient quantity to precipitate nearly all the lead, is run in from a burette. The liquid is boiled until the precipitate becomes orange-coloured, after which the titration is finished, the final point being indicated by contact with silver nitrate as an outside indicator on a white plate.

---

[1] See A. H. Low, *Technical Methods of Ore Analysis.*

[2] *J. A. C. S.*, 1897, **19**, 389.

The precautions to be observed are :—

The solution of the lead salt must be as concentrated as possible, and decidedly acid with acetic acid. There must be absence of other metals, especially such as can exist in lower forms of oxidation. Antimony and tin, unless thoroughly oxidized, and bismuth are particularly to be avoided. During titration the solution should be kept as near the boiling-point as possible. The strength of the dichromate solution should not vary much from that given above, nor should the solution of silver nitrate.

In the case of dealing with ores containing small quantities of silver, it is desirable to precipitate this before filtration with a little solution of sodium chloride. In this case it is well to employ larger drops of the silver nitrate used as indicator.

The method is specially suitable for such substances as white lead, red lead, litharge, etc. Red lead is dissolved by treating it with nitric acid, and adding a dilute solution of oxalic acid drop by drop until the lead oxide is completely dissolved. If organic matter is present the solution should be filtered before titration. White lead can be dissolved directly in acetic acid, and the solution titrated without filtration. In the case of white lead ground in oil, the sample should be dissolved in dilute nitric acid, the solution boiled, filtered, ammonia added in excess, and then an excess of acetic acid. The method can also be used with ingot lead, and alloys containing tin and antimony, but the sample must be thoroughly oxidized by repeated evaporation with fuming nitric acid, and the solution filtered before titration.

The lead in solution, after addition of ammonium or sodium acetate, may be precipitated by excess of $^{N}/_{10}$ dichromate solution. After boiling for a minute or two the precipitate is quickly filtered off, well washed, and the excess of dichromate in the cooled filtrate titrated with standardized ferrous ammonium sulphate solution and potassium ferricyanide as external indicator. Or the excess of dichromate in the filtrate may be determined iodimetrically by addition of potassium iodide and titration with sodium thiosulphate.

Lead in various Ores.—An investigation of many methods of determining this metal has been carried out by J. C. Bull.[1] The best results, including the foregoing dichromate process, were obtained by the molybdate and the ferrocyanide methods. The initial procedure in all the trials was to separate the lead as sulphate, which contained also gangue and other insoluble sulphates, by treating the ore with nitric or nitro-hydrochloric acid, evaporating with sulphuric acid and filtering off from soluble sulphates after being diluted.

Alexander's Molybdate Method[2].—The mixture of lead sulphate and impurities, obtained as above, is boiled for at least 10 minutes with ammonium acetate solution; the solution is then acidified with acetic acid, diluted to 200 c.c., again boiled, and a standard ammonium molybdate solution added until all the lead is precipitated. The end-point is ascertained by shaking the solution vigorously, allowing it to stand for a few minutes, and testing 1 drop of the clear liquid with 1 drop of a solution of 1 part tannin in 300 parts water and 1 drop of a lead solution; the appearance of a yellow colour indicates the presence of ammonium molybdate in excess. The molybdate solution is prepared by dissolving 9 gm. of the salt in 1 litre of water and standardizing against lead sulphate. Since the indicator is not very sensitive, requiring about 0·8 c.c. of molybdate to affect it, a blank must be made to ascertain the correction due to this. This method gave very good results when tried on the ores; the presence of antimony, bismuth, and calcium had no effect on it; but in the presence of barium and, to a lesser extent, strontium, it gave low results.

---

[1] *Analyst*, 1903, **28**, 15.

[2] See *J. C. S.*, 1893, **64**, 599. See also A. H. Low, *Technical Methods of Ore Analysis.*

Beebe's Ferrocyanide Method[1].—The mixture containing the lead sulphate is gently heated to boiling with 10 c.c. of a saturated solution of ammonium carbonate. After cooling, the precipitate is transferred to a filter, thoroughly washed, and then placed with the filter-paper in a flask containing a hot mixture of 5 c.c. glacial acetic acid and 25 c.c. water. This is boiled until the lead carbonate has dissolved, diluted to 150 c.c., heated to 60° C., and titrated with standard 1 per cent. potassium ferrocyanide solution, drops of uranium acetate solution placed on a white tile being used as indicator. Here also the correction due to the indicator must be determined. This method also gave very good results when no interfering metals were present.

4. Lead in Citric and Tartaric Acids, and in Cream of Tartar.—Warington[2] has worked out the best method of ascertaining the proportions of lead in these commercial acids, and shows that ammonium sulphydrate is to be preferred to sulphuretted hydrogen for the process, inasmuch as the tint produced is much more uniform throughout a long scale, and very free from turbidity. Warington's description of the method is as follows:—

The depth of tint produced for the same quantity of lead present is far greater in an ammoniacal tartrate or citrate solution than in the same volume of water; it is quite essential, therefore, if equality of tint is to be interpreted as equality of lead, that all comparisons should be between two citrate and tartrate solutions, and not between one of these and water.

To carry out the method it is necessary to have solutions of lead-free tartaric and citric acids supersaturated with pure ammonia; these solutions should develop no colour when treated with ammonium sulphydrate. A convenient strength is 100 gm. of acid in 300 c.c. of final solution.

The standard lead solutions are made by dissolving 1·6 gm. of crystallized lead nitrate dried over sulphuric acid in a litre of water, each c.c. = 0·001 gm. Pb. A solution made by diluting 100 c.c. of this to a litre is that actually used, 1 c.c. = 0·0001 gm. Pb.

Of the tartaric or citric acid to be examined, 40 gm. are taken and dissolved in a little water; warm water is most convenient for crystal and cold for powder; the solution is best prepared in a flask. To the cold solution pure strong ammonia is gradually added till it is in slight excess; the final point is indicated in the case of tartaric acid by the solution of the acid ammonium tartrate first formed; in the case of citric acid it is conveniently shown by a fragment of turmeric paper floating in the liquid. When an excess of ammonia is reached the liquid is cooled, diluted to 120 c.c., and filtered.

---

[1] See *C. N.*, 1896, **73**, 18.

[2] *J. S. C. I.*, 1893, **12**, 97, 222.

As a preliminary experiment 10 c.c. are taken, diluted to 50 c.c. in the measuring cylinder, and placed in a nesslerizing glass, one drop of ammonium sulphydrate solution added, and the whole well stirred; the colour developed indicates what volume of solution should be taken for the determination—this volume may range from 5 c.c. to 50 c.c. If less than 50 c.c. are taken the volume is brought to 50 c.c. with water, and one drop of ammonium sulphydrate is then added.

The tint thus produced has now to be matched with the pure solutions. A volume of the pure ammoniacal tartrate or citrate, identical with that taken of the acid under examination, receives a measured quantity of lead solution from the burette, the volume is brought to 50 c.c., it is placed in a nesslerizing glass, and receives one drop of ammonium sulphydrate; the experiment is repeated till a match is obtained. As in the previous method, the best comparison of tints is obtained by making finally three simultaneous experiments, one with the acid under examination, the other two with pure acid containing slightly varying amounts of lead, the aim being that the tint given by the acid to be analysed shall lie within this narrow scale. In following this method, considerable use has to be made of the weaker of the two lead solutions already mentioned.

The whole time required for a determination of lead by this method now given is about 1½ hours: this time will be somewhat shortened as the operator becomes familiar with the tints produced by varying proportions of lead. If traces of copper or iron are present, any interference on their part may be removed by adding to the alkaline solution a few drops of potassium cyanide solution.

The following method answers well, and has the advantage that only 10 gm. of sample are used.

Solutions required.—(*a*) Standard lead solution. A strong solution is first made by dissolving 0·16 gm. of lead nitrate crystals in water and diluting to 100 c.c. The solution used as a standard is made by diluting 10 c.c. of this strong solution to 100 c.c., and of this,

$$1 \text{ c.c.} = 0{\cdot}0001 \text{ gm. Pb.}$$

(0·1831 gm. of lead acetate crystals dissolved in water and diluted to 1 litre give a solution of the same strength).

(*b*) Potassium cyanide[1].—10 per cent. solution in water (the B.P. recommends the addition of 2 c.c. of hydrogen peroxide solution (10 vol.)).

(*c*) Ammonia.—10 per cent. solution, made by diluting 0·88 ammonia with twice its volume of water.

(*d*) Sodium sulphide.—10 per cent. solution, or
Ammonium sulphide (see note below).

---

[1] Potassium cyanide is used to eliminate the effect of any copper and iron that may be present in the substances tested.

METHOD OF PROCEDURE.—(i) Cream of Tartar.—10 gm. are treated with about 70 c.c. of hot water and 15 c.c. of ammonia, and stirred till dissolved. The solution is made up to 100 c.c. and filtered through a dry filter. To the filtrate 5 or 6 drops of KCy followed by 2 or 3 drops only of sodium sulphide, are then added.

(ii) Tartaric acid.—Dissolve 10 gm. in about 40 c.c. of hot water, add 5 or 6 drops of KCy solution, then 25 c.c. of ammonia, which should make the solution ammoniacal, and finally 2 or 3 drops only of sodium sulphide. Make up to 100 c.c.

(iii) Citric acid.—10 gm. are treated exactly as in (ii), except that 30 c.c. of ammonia are used instead of 25 c.c. (adding the reagents in the same order).

The 100 c.c. of solution obtained in each case is then nesslerized against a standard solution made by treating 10 gm. of a lead-free acid (tartaric or citric, as the case may be) in exactly the same way, adding to it 2 c.c. of standard lead solution (*a*). If the acid being tested gives an appreciably darker colour than the standard, a smaller quantity of it should be taken and treated similarly. A darker standard should not be used.

Note.—In place of sodium sulphide W. A. Davis prefers freshly made colourless ammonium sulphide, prepared by diluting 2 c.c. of 0·88 ammonia to 10 c.c. and saturating with well-washed H_2S.

Dr. MacFadden in a report to the Local Government Board[1] recommends the adoption of a limit of 0·002 per cent. (approximately 1/7th grain per lb.) of lead as impurity in tartaric and citric acids and cream of tartar.

5. Colorimetric Determination in Water.—When there is no heavy metal except lead present, simple addition of freshly made sulphuretted hydrogen water in the presence of weak acetic acid as suggested by Miller gives good results, comparison being made with standard lead solution (*a*) given above. The determination is made in colourless glass cylinders in the same way as described for copper (p. 216), or iron (p. 245), taking care that the comparative tests are made under precisely the same conditions.

Detection and Colorimetric Determination of Lead, Copper and Zinc in Water Supplies.—L. W. Winkler[2].—The sensitiveness of the H_2S test for lead, whether in alkaline or acetic acid solution, is increased by the presence of ammonium chloride. Two portions of 100 c.c. each of the water are measured out. To one portion are added 2 c.c. of 10 per cent. acetic acid, 2 gm. ammonium chloride, and 2 or 3 drops of 10 per cent. sodium sulphide solution. To the other portion 2 or 3 drops of 10 per cent. potassium cyanide solution are added, to convert ferrous iron to ferro-cyanide and prevent the precipitation of copper as sulphide, then after 2 or 3 minutes 2 gm. ammonium chloride, followed by 5 c.c. of 0·96 ammonia and 2 or 3 drops of the sulphide reagent. In the absence of copper the two solutions are nearly equal in tint, but if both metals are present the acid solution is the darker, whilst if copper alone is present the alkaline solution is nearly colourless. By the use of ammonium chloride, as detailed above, it is unnecessary to make a number of standards, when making colorimetric determinations, since exactly the same tint is obtained by running a standard lead solution from a burette into a sulphide solution as by adding the sulphide to an equal quantity of lead solution previously diluted. (Standard lead nitrate solution 0·1599 gm. per litre, 1 c.c. = ·0001 gm. Pb.)

---

[1] Report (No. 2) on Lead and Arsenic in Tartaric acid, Citric acid, and Cream of Tartar, 1907.

[2] *Z. angew. C.*, 1913, **26**, 38, also *Analyst*, 1913, **38**, 123, and *J. S. C. I.*, 1913, **32**, 157.

In absence of lead, copper is best determined colorimetrically as sulphide, again with the addition of ammonium chloride, which approximately doubles the intensity of the coloration.

But in the presence of lead it is determined by the ferrocyanide method (see page 215), after which the lead may be determined as follows: a few drops of 10 per cent. potassium cyanide solution are added to the water sample and the copper standard, when the red colour gives place to a yellowish green. This colour, which is equal in the two cylinders, does not interfere with the subsequent determination of the lead as sulphide. For full particulars as to determination of small quantities of zinc in water see *J. S. C. I.*, 1913, **32**, 157.

With respect to the amount of lead in a water-supply that may prove injurious, Prof. P. Frankland makes the following statement: "As regards the quantity of lead in water from which danger to health is to be apprehended, it is now generally admitted that water containing anything above $\frac{1}{20}$ of a grain of lead per gallon, or 0·07 part per 100,000, may, by continued use, produce mischief".

6. Colorimetric determination of Lead in the presence of Iron (for testing chemicals generally).—J. M. Wilkie[1] recommends the following procedure:—

A weighed portion of the substance is dissolved in water and the solution made distinctly acid by adding a few drops of acetic or other acid. 1 c.c. of 10 per cent. potassium cyanide solution is added, then a considerable excess of ammonia. If the solution is now colourless, it only remains to add a few drops of sodium sulphide solution and compare the colour produced with that developed by a solution containing a known amount of lead and treated precisely as detailed above. If the ammoniacal liquid is coloured, iron is present, and, if originally present in the ferrous state, it is only necessary to heat the solution to boiling, when the colour disappears, and on cooling to add the sulphide. When, however, ferric iron is present another portion of the substance must be dissolved, acidified, and a few drops of $^{N}/_{10}$ sodium thiosulphate added—the exact amount required depending on the amount of iron present. The solution is heated slowly to incipient boiling, allowed to stand until the colour suddenly disappears, and then potassium cyanide, etc., added as usual.

Note.—According to E. Eegrive,[2] potassium dichromate shows 1 gm. of lead in 2,100,000 c.c., and sodium sulphide 1 gm. in 2,840,000 c.c., both tests being made by diluting neutral aqueous solutions of lead nitrate.

---

[1] *J. S. C. I.*, 1909, **28**, 636, and 1910, **29**, 7.

[2] *Ibid.*, 1914, **33**, 891.

MAGNESIUM.

Mg = 24·32.

An alkalimetric process for the determination of this substance has been adopted by Stolba, a reference to which is made under Phosphoric Acid, p. 121, but the time and trouble required to wash out the ammonia by alcohol renders the method too difficult for general purposes. A much shorter procedure has been devised by R. K. Meade.[1]

The method is based on the same principles as Williamson's process described under "Arsenic," p. 162. He found that when a solution of arsenic acid contained sufficient sulphuric or hydrochloric acid the arsenic is quickly reduced to arsenious acid even in the cold. For every molecule of arsenic acid so reduced there corresponds two atoms of magnesium, and two molecules or four atoms of iodine are liberated. This latter is titrated with sodium thiosulphate, and from the volume of standard solution required the magnesium is calculated.

The standard solutions are conveniently made as follows:—

Standard sodium arsenate is prepared by dissolving 12·29 gm. of pure arsenious acid in nitric acid, evaporating on a water-bath to dryness, neutralizing with sodium carbonate in solution, and when dissolved making up to a litre with distilled water. Each c.c. = 0·005 gm. of Mg.

The standard solution of sodium thiosulphate is made to correspond to this either by direct titration, or by making it equal to a standard iodine solution made by dissolving 52·24 gm. of pure iodine, and 75 gm. of potassium iodide in about 200 c.c. of water, and making up to 1 litre. Each c.c. = 0·005 gm. Mg.

Method of Procedure: Pour the magnesia solution, which should not contain too great an excess of ammonium chloride or oxalate, into a conical flask or a gas-bottle of sufficient size. Add one-third the volume of the solution of strong ammonia and 50 c.c. of sodium arsenate. Cork up tightly and shake vigorously for 10 minutes. Allow the precipitate to settle somewhat, then filter and wash with a mixture of water and strong ammonia (3 : 1) until the washings cease to react for arsenic; avoid, however, using an excess of the washing fluid. Dissolve the precipitate in dilute hydrochloric acid (1 : 1), allowing the acid solution to run into the flask in which the precipitation was made, and wash the filter-paper with the dilute acid, until the washings and solution measure 80 or 100 c.c. Cool, and add from 3 to 5 gm. of potassium iodide, free from iodate; allow the solution to stand for a few minutes, and then run in the standard thiosulphate until the colour of the liberated iodine fades to a pale straw colour. Add starch, and titrate until the blue colour of the iodide of starch is discharged. If preferred, an excess of thiosulphate may be added, then starch and standard iodine until the blue colour is produced. On adding the iodide of potassium to the acid solution, a brown precipitate forms, which, however, dissolves when the thiosulphate is added

---

[1] *J. A. C. S.*, 1899, **21**, 746.

Experience has proved that the whole process can be done within an hour, and the results in the case of dolomite, limestone, slag and cement are very near those given by gravimetric methods.

Frankforter and Cohen[1] state that a much sharper end-reaction is obtained if starch indicator is not used. They apply the process to the **determination of magnesium in water,** thus:—

500 c.c. of the water, after removal of iron and calcium as usual, are acidified, evaporated to 100 c.c., 33 c.c. of strong ammonia and 25 c.c. of a 10 per cent. solution of sodium arsenate added, and the flask shaken vigorously for 10 minutes. The precipitate is filtered off, washed with the least possible amount of dilute ammonia, dissolved in 25 c.c. dilute sulphuric acid (1 : 4) into the original flask, the filter washed with 50 c.c. hot water, and 10 c.c. sulphuric acid (1 : 1) added. After cooling, 3·5 gm. of potassium iodide are added, the solution allowed to stand for 5 minutes, then the liberated iodine titrated with thiosulphate without starch indicator.

For the determination of **magnesium in water analysis** in the solution remaining after precipitation of the calcium, F. W. Bruckmiller[2] recommends the following methods. (*a*) The solution is evaporated to dryness, and ammonium salts decomposed by heating. The residue is dissolved in a small volume of water, acidified with hydrochloric acid, and after filtering, made slightly alkaline with ammonia. Microcosmic salt solution is slowly added to the cold solution, with stirring, and after the precipitate has formed a quantity of ammonia solution, equal to one-third of the total volume added, is introduced, and the solution allowed to stand 18 hours. The precipitate is filtered off with the aid of suction and washed with 25 c.c. of alcohol. After transferring with hot water to a beaker, a known excess of $^N/_{10}$ hydrochloric acid is added and the excess titrated back with $^N/_{10}$ sodium hydroxide, using methyl orange as indicator.

(*b*) The solution is entirely freed from ammonium salts by evaporation and ignition, the residue dissolved in a small quantity of hydrochloric acid, and the solution filtered. The solution is cooled, made alkaline with ammonia, which is free from ammonium salts, and an excess of 10 c.c. added. A 10 to 20 per cent. excess of sodium arsenate is added slowly and with vigorous stirring which is continued for about 10 minutes after no further precipitation has taken place. The solution is allowed to stand in a cool place to allow the precipitate of magnesium ammonium arsenate to settle, and, after filtering and washing with 3 per cent. ammonia water, the precipitate is dissolved in hot water, and 10 c.c. of concentrated hydrochloric acid and 0·3 gm. potassium iodide added for every 100 c.c. of liquid. The liberated iodine is titrated with $^N/_{10}$ thiosulphate.

(*c*) The precipitate of magnesium ammonium arsenate obtained as in (*b*), after washing with dilute ammonia, is dissolved in hot water and the solution transferred to an Erlenmeyer flask fitted with a trap. An excess of potassium iodide and 10 c.c. of sulphuric acid (1 : 1) are added and the whole boiled rapidly until iodine vapours are no longer visible.

---

[1] *J. A. C. S.*, 1907, **29**, 1464.

[2] *Ibid.*, 1907, **39**, 610.

While still hot, the trace of iodine remaining is destroyed with sulphurous acid and the whole cooled quickly. The acid solution is neutralized with $^N/_{10}$ sodium hydroxide, using phenolphthalein as indicator, and adding from time to time a solution of sodium phosphate. When titration is complete, the volume of phosphate solution added should be equal to one-half the volume of the iodine solution The total volume should be about 250 c.c., and if greater than this more phosphate must be added in proportion to keep the hydrogen ion concentration at the right value. For every 100 c.c. of $^N/_{10}$ iodine, 11 gm. of Na_2HPO_4, $12H_2O$ is necessary in a volume of 250 c.c. The arsenious acid is titrated as usual with $^N/_{10}$ iodine.

P. L. Hibbard[1] has proposed a modification of the above procedure for small amounts of magnesium, 5 to 0·1 mgm.

MANGANESE.

Mn = 54·93, MnO = 70·93, MnO_2 = 86·93.

Factors.

Metallic iron × 0·6350 = MnO.
" " × 0·4918 = Mn.
" " × 0·7783 = MnO_2.
Ferrous Ammonium Sulphate × 0·0907 = MnO.
" " " × 0·1112 = MnO_2.
Cryst. oxalic acid × 0·6896 = MnO_2.

1 c.c. $^N/_{10}$ solution = 0·003547 gm. MnO or = 0·004347 gm. MnO_2.

All the oxides of manganese, with the exception of the first or protoxide, when boiled with hydrochloric acid, yield chlorine in the following ratios :—

Mn_2O_3 = 1 eq. O = 2 eq. Cl.
Mn_3O_4 = 1 eq. O = 2 eq. Cl.
MnO_2 = 1 eq. O = 2 eq. Cl.
MnO_3 = 2 eq. O = 4 eq. Cl.
Mn_2O_7 = 5 eq. O = 10 eq. Cl.

The chlorine so produced can be allowed to react upon a known weight of ferrous salt; and when the reaction is completed, the unchanged amount of iron salt is determined by permanganate or dichromate.

Or, the chlorine may be led by a suitable arrangement into a solution of potassium iodide, there setting free an equivalent quantity of iodine, which is determined by the aid of sodium thiosulphate.

Or, in the case of manganese ores, the reaction may take place with oxalic acid, resulting in the production of carbonic acid, which can be weighed as in Fresenius and Will's method, or the amount of unchanged acid remaining after the action can be found by permanganate.

The largely increased use of manganese in the manufacture of steel has now rendered it imperative that some rapid and trustworthy methods of determination should be devised, and this has been done by well-known chemists. The first method described appears to have been simultaneously suggested by Pattinson and Kessler; both have succeeded in finding a method of separating manganese as dioxide of perfectly definite composition. Pattinson[1] found that the regular precipitation was secured by ferric chloride, and Kessler by zinc chloride. Wright and Menke have experimented on both processes with equally satisfactory results, but give a slight preference to zinc. Pattinson titrates the resulting MnO_2 with standard dichromate, and Kessler with permanganate.

---

[1] *J. Ind. Eng. Chem.*, 1919, 11, 753; (abstr.) *J. S. C. I.*, 1919, 38, 797A.

1. Precipitation as MnO_2 and Titration with Dichromate (Pattinson).

The author's own description of the method is as follows:—

This method depends upon the whole of the manganese being precipitated as hydrated dioxide by calcium carbonate when chlorine or bromine is added to a solution of manganous salt containing also a persalt of iron or a salt of zinc, and under certain conditions of temperature, etc. This method is used for determining manganese in manganiferous iron ores, manganese ores, spiegeleisen, ferromanganese, etc.

METHOD OF PROCEDURE: A quantity of the sample to be analysed, containing not more than about 0·25 gm. of manganese, is dissolved in hydrochloric acid. In the case of spiegeleisen and ferromanganese, about 3 to 4 c.c. of nitric acid are afterwards added to oxidize the iron. In the case of manganese ores, ferromanganese, and manganese slags, which do not contain as much iron as manganese, there is added to the solution as much iron, in the form of ferric chloride, as will make the quantities of iron and manganese in the solution about equal. An excess of iron is no drawback, except that a larger precipitate has afterwards to be filtered and washed.

The excess of acid in the solution is then neutralized by the addition of calcium carbonate, which is added until a slight reddening of the solution is produced. The solution is then rendered very slightly acid by dropping into it just enough hydrochloric acid to remove the red colour.

Then add in all cases 30 c.c. of a solution of zinc chloride containing 0·5 gm. of metallic zinc. The liquid is then brought to the boiling point, and diluted with boiling water to about 300 c.c.

60 c.c. of a solution of calcium hypochlorite, made by dissolving about 33 gm. of bleaching powder per litre and filtering, are then poured into the manganese solution; but to the hypochlorite solution, before pouring it into the manganese solution, there should be added just enough hydrochloric acid to give it a faint permanent greenish-yellow colour after gentle agitation.

The object of this addition of acid is to prevent a precipitate forming when the hypochlorite is added, due to the alkalinity of this solution. When hydrochloric acid is added in this way to the solntion of calcium hypochlorite, the manganese solution remains clear on the addition of the calcium hypochlorite, and any possible local precipitation of manganese in a lower state of oxidation than MnO_2 is obviated.

---

[1] *J. S. C. I.*, 1891, **10**, 337.

Finally, add to the manganese solution about 3 gm. of calcium carbonate diffused in about 15 c.c. of boiling water. After the first evolution of carbonic acid has ceased, during which time the cover is kept on the beaker, the precipitate is stirred to make it collect together, and 2 c.c. of alcohol or methylated spirit are added and it is again stirred.

The precipitate is then thrown upon a large filter and washed, at first with cold water until the greater part of the chlorine is removed, and afterwards, to make the washing more rapid, with warm water at about 155° F. (65° C.). It is washed until, after draining, a drop shaken down straight from the precipitate by gently jolting the funnel shows no indication of chlorine when tested with a strip of iodized starch-paper. As a matter of practice two or three washings are given after there has ceased to be any indication of chlorine.

By carrying out the process in the manner here described, the temperature of the liquid, immediately after the precipitation is complete, is about 170° F. (77° C.), and it is found that the best and most constant results are obtained when the temperature after precipitation is near this point.

70 c.c. of an acidified solution of ferrous sulphate, containing about 0·7 gm. of iron, and made by dissolving crystallized ferrous sulphate in a mixture of 1 part of monohydrated sulphuric acid and 3 parts of water, are then accurately measured off by a pipette and run into the beaker in which the precipitation was made. The filter paper, together with the precipitate, is then removed from the funnel and placed in the solution of ferrous sulphate in the beaker. The precipitate readily dissolves even in the cold (sometimes it may be necessary to add a little more acid to dissolve the ferric hydrate completely), the manganese dioxide converting its equivalent of ferrous sulphate into ferric sulphate. A sufficient quantity of cold water is now added, and the ferrous sulphate still remaining is titrated with a standard solution of potassium dichromate.

The exact amount of ferrous sulphate in 70 c.c. of the ferrous sulphate solution is determined by measuring off into a clean beaker another portion of 70 c.c. and titrating with standard dichromate solution. The difference between the amounts of that solution required gives the quantity of ferrous sulphate oxidized by the manganese dioxide, and from this the percentage of manganese in the sample can be calculated.

The ferrous sulphate solution should be standardized from day to day, as it undergoes slow oxidation on exposure to air.

A solution of bromine in water may of course be used instead of the hypochlorite solution, in which case no acid is added to the bromine solution. When using bromine, a solution containing about 0·7 gm. of bromine (about 22 gm. per litre) should be used, and 90 c.c. of this solution used for precipitating about 0·25 gm. of manganese.

The unpleasantness of working with bromine may be mitigated, to some extent, by adding to the bromine solution, before pouring it into the liquid containing the manganese, a few drops of a solution of sodium hydrate until nearly all, but not quite all, the bromine is taken up. If an excess of sodium hydrate were added to the bromine it would produce a precipitate on pouring it into the manganese solution, and this is to be avoided.

It is preferable to have both zinc and iron in solution with the manganese. When working with either of these alone all the manganese is obtained in the form of dioxide, but with iron alone there is a greater tendency to the formation of permanganate than when zinc is also present. This point was also noticed by Wright and Menke.[1] When zinc alone is present, it is found that the precipitation of the dioxide does not take place so rapidly as when iron is also present. When both iron and zinc are used, there is very seldom any permanganate formed, if care is taken not to use an unnecessarily large excess of chlorine or bromine, but occasionally there is a small quantity formed, especially if the precipitate is left to stand some considerable time before filtering. It was found that the addition of a very small quantity of alcohol immediately after the precipitation of the manganese is complete entirely prevents the formation of permanganate even when a large excess of chlorine has been used, and for this reason it is well to add it.

When filtering paper has been wetted with the solution containing free chlorine or bromine and afterwards washed clean, it has no reducing action either upon potassium dichromate or upon ferric sulphate. The addition of the filter together with the precipitate to the solution of ferrous sulphate, therefore, does not influence the result.

It must be pointed out that the presence of lead, copper, nickel, cobalt, and chromium in the substances under examination interferes with the accuracy of this method of titrating manganese.

It was found that so large a proportion as 1 per cent. of lead, copper, and nickel does not greatly interfere with the test, but the interference of cobalt, and especially of chromium, is serious. All these substances, except chromium, form, under the conditions of the test, higher oxides insoluble in water, which are precipitated with the manganese dioxide, and which oxidize ferrous sulphate to ferric sulphate; whilst chromium forms some insoluble chromate which goes down with the manganese dioxide.

Fortunately these metals rarely, if ever, occur in the ores of manganese or in spiegeleisen and ferromanganese in sufficient quantity to affect the practical accuracy of this test.

This volumetric method cannot, however, be applied to the determination of manganese in alloys of these metals, such as ferrochrome or in ores containing these metals, without previously separating them from the solution containing the manganese.

1 c.c. $^{N}/_{10}$ dichromate = 0·002747 gm. Mn.

Saniter[2] in criticizing the method gives it the credit for yielding slightly low results, and advocates the standardizing of the dichromate, not upon iron, but upon a manganese oxide of known composition.

Pattinson prefers to use bleach solution to bromine, because the formation of permanganate is more easily seen. In any case not more than a trace of permanganate should be formed, and if the first experiment shows this to be the case, another trial must be commenced with less oxidizing material.

---

[1] *J. C. S. Trans.*, 1883, 43.

[2] *J. S. C. I.*, 1894, **13**, 112.

J. W. Westmoreland describes a modified method which is designed to overcome some objections raised against the above processes.

With ferro-manganese and ores containing about 50 to 60 per cent. of Mn, about 0·4 gm. is taken ; ores with 40 per cent., 0·5 gm. ; manganiferous iron ores, with say about 20 per cent. each of Fe and Mn, 0·75 gm. ; spiegeleisen and silicospiegels, with about 25 per cent. Mn, the same.

The material, having been brought into solution by any of the methods described, is concentrated to a small bulk in a large conical beaker. A solution of ferric chloride, containing about the same amount of iron as there is approximately of Mn, is added, together with a solution of zinc chloride, containing about 0·5 gm. of Zn. The excess of acid is then neutralized with caustic potash, so that the bulk of liquid is about 80 c.c. To this is added about 60 c.c. of saturated bromine water (more for ferro-manganese, less for manganiferous iron ores) and zinc oxide emulsion[1] is gradually dropped in with shaking, until the Fe and Mn are precipitated (care must be taken to avoid a large excess of zinc oxide). The beaker is then filled up with boiling tap-water, and the clear liquid poured through a filter, previously adding a few drops of alcohol. The beaker is then filled with boiling water five times in succession, the precipitate being stirred up with the hot water each time of washing and allowed to settle. It is then brought on the filter, and again freely washed with boiling distilled water. The filter and contents are then transferred to the beaker, an excess of acid solution of ferrous sulphate added, and when the precipitate is dissolved the liquid is diluted with cold distilled water, and the excess of ferrous iron determined at once with permanganate. The value of the iron solution in metallic iron is found by titrating the same volume of iron solution as has actually been used for dissolving the Mn precipitate, and the Fe oxidized multiplied by 0·4918 = Mn.

It is absolutely necessary, in order to get accurate results, to wash the precipitate as thoroughly as is here insisted upon.

$$2KMnO_4 + 3MnO = K_2O + 5MnO_2$$

$$1 \text{ c.c. } {}^{N}/_{10} \text{ permanganate} = \cdot 001648 \text{ gm. Mn.}$$

---

[1] The emulsion of zinc oxide may, of course, be readily made by rubbing down pure zinc oxide in water so as to be of about the consistence of cream. Emmerton (*Trans. Amer. Inst. Min. Eng.*, **10**, 201), suggests the following method of preparing this reagent. Dissolve ordinary zinc white in HCl, add the powder until there remains some undissolved, then add a little bromine water ; heat the mixture, filter and precipitate the zinc oxide from the filtrate with the slightest possible excess of ammonia. Wash thoroughly by decantation, and finally wash into a bottle with approximately enough water to give a proper consistence. By this method a very finely divided oxide is obtained, owing to its not being dried.

2. Volhard's Permanganate Method.[1]

This method consists in titrating a hot solution of manganous sulphate, containing zinc sulphate, with potassium permanganate, when MnO_2 is precipitated, the reaction being essentially as follows:—

$$3MnSO_4 + 2KMnO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + H_2SO_4.$$

Hence, 1 c.c. $^{N}/_{10}$ permanganate = 0·001648 gm. Mn. The method has been the subject of numerous modifications.[2] The details of the original process are as follows:—

A quantity of material is taken so as to contain from 0·3 to 0·5 gm. Mn, dissolved in hydrochloric or nitric acid, evaporated in porcelain to dryness, first adding a little ammonium nitrate, then heated over the flame to destroy organic matter. The residue is digested with HCl, a little strong H_2SO_4 added, and again evaporated to dryness, first on the water-bath, then with greater heat till vapours of SO_3 are evolved. It is then washed into a litre flask and neutralized with sodium hydrate or carbonate; sufficient pure zinc oxide, made into a cream, is added to precipitate all the iron. The flask is filled to the mark, shaken, and 200 c.c. filtered off into a boiling flask, acidified with 2 drops of nitric acid (sp. gr. 1·2), heated to boiling, and titrated with $^{N}/_{10}$ permanganate while still hot. Owing to the presence of the trace of nitric acid, most operators now deduct 0·2 c.c. of permanganate before calculating the manganese.

Särnström's method of using this process for determining manganese in iron ores, as described by Mixer and Du Bois, is to precipitate the iron in hot dilute solution by sodium carbonate, care being taken to add no more than is just sufficient to precipitate the iron; then titrating (without filtering off the ferric oxide) with permanganate. Using the soda in this way does not give perfect neutralization, yet it gives excellent results, as shown by both Mixer and Du Bois and G. Auchy. This is difficult to explain, as mentioned by the latter chemist, because in working either Volhard's method or Stone's modification of it, there must be a much larger quantity of zinc emulsion used than is necessary to precipitate the iron, in order to avoid too high results. But all experiments show that Särnström's process is quite free from this error. Auchy is of opinion that either the ferric oxide, by its presence, in some way prevents high results being obtained when solutions are incompletely neutralized, or by its presence prevents the precipitation of manganese dioxide, unless the solution be exactly neutralized when titrated; the permanganate simply colouring the solution, and no manganese being precipitated unless more sodium carbonate is added.

G. E. Stone's modification of the original Volhard's method gives an easier and quicker result, as no evaporation with sulphuric acid is needed, and the precipitate of ferric oxide rapidly subsides in the faintly acid nitric acid solution.

---

[1] *Annalen*, 1879, **198**, 318.

[2] Modifications of Volhard's original method have been discussed by
Mayer, *Z. angew. Chem.*, 1907, **21**, 1980, and *Analyst*, 1908, **33**, 34;
Heike, *Stahl u. Eisen*, 1909, 1921, and *J. S. C. I.*, 1910, **29**, 114;
Deiss, *Chem. Zeit.*, 1910, 237, and *J. S. C. I.*, 1910, **29**, 456;
Fischer, *Z. anal. Chem.*, 1909, **48**, 751, and *J. S. C. I.*, 1910, **29**, 47.

METHOD OF PROCEDURE: The necessary precautions, as given by G. Auchy, are printed in italics. 3·3 gm. of drillings are dissolved in 50 c.c. of nitric acid (sp. gr. 1·20) and washed into a 500 c.c. measuring flask. Two-thirds of the amount of sodium carbonate solution necessary for complete neutralization are added, and the *liquid cooled.* Zinc oxide emulsion is then added until the solution stiffens, an *excess being avoided.* After dilution to about three-fourths the capacity of the flask the whole is allowed to stand until the ferric oxide begins to settle, and a *considerable excess of zinc oxide emulsion then added* to the colourless solution. After being made up to the mark and well shaken, the precipitate is allowed to settle, and 250 c.c. of the clear solution heated in a flask to boiling and titrated with permanganate of strength 0·0056. After making the necessary deductions for impurities in the sodium carbonate and zinc oxide (which have been previously ascertained), the number of c.c. of permanganate taken is divided by 10, and 0·02 *per cent. deducted* from the result.

W. Fischer's Modification of Volhard's Method.[1]—This modification is claimed to give accurate results in the presence of chlorides and when titrating with a solution of permanganate standardized by oxalic acid, without the use of a correcting factor. A solution of manganous salt, containing hydrochloric or sulphuric acid, is treated as follows:—

Sodium hydroxide is added until a slight precipitate appears; this is redissolved with a few drops of sulphuric acid, 1 gm. of freshly ignited zinc oxide and 10 gm. of zinc sulphate are added, and the solution is titrated with permanganate, with frequent boiling and shaking. *Then 1 c.c. of pure glacial acetic acid is added* and the liquid is boiled; this discharges the pink colour, apparently owing to the liberation of absorbed manganous salt from the precipitate, which becomes flocculent and settles, and the liquid is again titrated until the pink colour is restored, the total volume of permanganate used being taken as that required to react with the manganese. If sulphates only be present, about 10 gm. of zinc sulphate are added for every 10 c.c. of $^{N}/_{10}$ permanganate used. Iron when present, as in the analysis of ferromanganese, is, as usual, precipitated with zinc oxide, and manganese is determined in the filtrate.

Cahen and Little[2] have investigated this modification and find that it gives very consistent results.

3. Determination by Conversion into Permanganic Acid by means of Sodium Bismuthate.

The essential principle of the bismuthate process is the rapid and complete oxidation of a manganese salt to permanganic acid in cold nitric acid solution, and as there is no limit to the amount of manganese oxidizable the process is applicable to rich alloys. The bismuth in the reagent exists as the tetroxide, Bi_2O_4, and this compound furnishes the available oxygen. Sodium bismuthate has no fixed composition. The reaction that takes place is essentially as follows :—

---

[1] *Z. a. Chem.*, 1909, **48**, 751-760.

[2] *Analyst*, 1911, **36**, 52. This paper gives an interesting review of the whole subject.

$$2MnO + 5Bi_2O_4 = Mn_2O_7 + 5Bi_2O_3.$$

Reddrop and Ramage's Method (modified).[1]

Solutions required.—(i) Decinormal potassium permanganate. (ii) Decinormal solution of ferrous ammonium sulphate, made by dissolving about 40 gm. of the crystals in about 600 c.c. of water, adding 20 to 30 c.c. of strong sulphuric acid and making the cold solution up to 1 litre. The exact strength of the solution is determined from time to time by (i). 39·22 gm. of the crystals would give a solution of exact strength.

Reagent required.—Sodium bismuthate, which is made as follows: Heat 20 parts of sodium hydroxide in a nickel or iron dish until all the water is expelled and the material is nearly red hot. Add in small quantities 10 parts of bismuth subnitrate previously heated until all the water and nearly all the nitric acid have been driven off. To the fused mass add 3 parts of sodium peroxide and pour the brownish yellow fused material on an iron plate to cool. When cold, but before it begins to deliquesce, break it up and place it in a large jar of water to dissolve the excess of soda salts. Wash by decantation and finally on the pump in an alundum dish, or if this is not available, on a hard filter. Dry at a low heat and pass through a fine sieve.[2]

According to Blair the delicacy of the reaction of manganese in nitric acid solution with sodium bismuthate is such that 0·000005 gm. of manganese gives an appreciable colour in 50 c.c. of solution.

THE PROCESS: Exactly 1·1 gm. of the drillings are placed in a small flask and 30 c.c. of nitric acid (sp. gr. 1·2) added. When the violent action has subsided, heat to boiling on the hot plate and add from time to time a little sodium bismuthate in order to oxidize the carbonaceous matter. The amount of bismuthate required depends upon the amount of carbon in the sample, mild steels requiring only a few mgm., but hard steels, etc., considerably more. In any case the carbon must be completely oxidized by the bismuthate or grave errors will result. Most steels contain sufficient manganese to yield a permanent brown precipitate of hydrated peroxide of manganese when the oxidation of the carbonaceous matter is complete. This precipitate is then just dissolved by adding a few drops of sulphurous acid or ferrous sulphate solution and the flask at once cooled under the tap. 1½ to 2 gm. of bismuthate are added and the flask shaken several times during 3 minutes. Allow to settle. The strongly-coloured supernatant liquid is then carefully decanted on to an asbestos filter, the residue washed several times by decantation with 2 per cent. nitric acid, the washing being complete when the liquid comes through the filter perfectly colourless. Solution (ii) is now run into the above liquid, with shaking, until the dark liquid has become of a pale green colour.

N/10 permanganate is then added from a burette, a drop at a time, until a permanent pale pink coloration is produced.

---

[1] Arnold and Ibbotson's *Steel Works Analysis*, 3rd edition.

[2] Blair's *Chemical Analysis of Iron*, 8th edition, 1918.

The standardization of the ferrous solution is then effected by at once running in about 20 c.c. of it into the same flask without washing out the finished assay and again titrating with permanganate of exact strength.

1 c.c. $^{N}/_{10}$ ferrous ammonium sulphate = 0·0011 gm. Mn or 0·1 per cent. on 1·1 gm. of steel.

EXAMPLE : 20·2 c.c. of ferrous solution added as above required 20·8 c.c. of $^{N}/_{10}$ permanganate. Hence each c.c. of the former = $\frac{20{\cdot}8}{20{\cdot}2} = 1{\cdot}03$ c.c. of $^{N}/_{10}$ strength.

1·1 gm. of the sample required 10·6 c.c. of the ferrous solution, equal to 10·6 × 1·03 = 10·9 c.c. of exactly $^{N}/_{10}$ strength, and 0·35 c.c. permanganate as required to produce a pink coloration. Hence, 10·9 − 0·35 = 10·55 c.c. $^{N}/_{10}$ ferrous ammonium sulphate were used, equivalent to 1·055 per cent. Mn.

Chromium interferes with the above process, since the bismuthate added to the hot solution converts some of this element into chromic acid and thus leads to unduly high results being obtained. In such cases it is necessary to add rather more sulphurous acid than is just required to clear the precipitated manganese peroxide, thus reducing the chromic acid again. After cooling, the process is carried through as rapidly as possible, when the amount of chromium oxidized in the time occupied is negligible. Demorest[1] states that if the permanganic acid solution obtained by the oxidation with bismuthate be titrated directly with sodium arsenite solution, any chromic or vanadic acid which may be present has no influence on the results.

Metzger and McCrackan[2] Modification of the Bismuthate Method.—This depends on the fact that, in hot sulphuric acid solution, sodium bismuthate oxidizes manganese to the quadrivalent condition (not to permanganate), and to the further fact that in cold sulphuric acid solution the oxidizing power of sodium bismuthate is so restricted, that it is unnecessary to remove the excess of bismuthate from the cooled solution by filtration before proceeding to the titration of the quadrivalent manganese.

METHOD OF PROCEDURE : To the manganese solution 10 to 15 c.c. of sulphuric acid are added, together with sufficient water to bring the volume up to 60 or 70 c.c. The mixture is allowed to cool, and then 1 to 2 gm. of sodium bismuthate are introduced into the flask in such a way that none sticks to the neck or sides. The flask is placed in a cold-water bath, which is then heated to boiling, and kept boiling for 20 minutes. The contents of the flask are cooled under the tap, a measured amount of standard ferrous sulphate solution, more than sufficient to react with the quadrivalent manganese, is added, the solution diluted to 200 c.c., and the excess of ferrous sulphate determined by titration with permanganate. Mn = 2Fe. The extreme error of the method is 0·3 c.c. of $^{N}/_{10}$ solution, and manganese is never over-estimated.

---

[1] *J. Ind. Eng. Chem.*, 1912, 4, 19

[2] *J. A. C. S.*, 1910, 32, 1250.

4. Colorimetric Method of Determination of Minute Quantities of Manganese by Conversion into Permanganate (Persulphate Method).[1]

This oxidation, which was formerly brought about by means of lead peroxide in presence of nitric acid (Walter Crum, 1845) was found by H. Marshall to be effected with certainty, with the production of a clear solution, by ammonium persulphate in the presence of a trace of a silver salt. This idea has been applied practically to samples of steel, pig iron and cinders by H. E. Walters, whose scheme is as follows :—

Solutions required.—(*a*) Silver nitrate solution, containing 1·33 gm. per litre; best made by dissolving 33·25 gm. of the salt in 500 c.c. of water and diluting 10 c.c. of this to 500 c.c. to form the solution to be used. (*b*) Ammonium persulphate. The salt acts best when slightly damp. Walters adds 10 c.c. of water to each 1 lb. bottle of the dry salt and mixes intimately.

METHOD OF PROCEDURE: 0·2 gm. of the steel to be tested and the same quantity of a standard steel of known manganese content, are weighed out and put into test-tubes 8 inches by 1 inch, and 10 c.c. of nitric acid (sp. gr. 1·2) are added to each. The tubes are placed in a water-bath and heated until solution is complete and all nitrous fumes have been driven off. 15 c.c. of silver nitrate solution (*a*) are added to each tube in the bath, followed immediately by about 1 gm. of ammonium persulphate, the tube being heated for about half a minute after oxidation has commenced. The tubes are removed from the bath while the evolution of oxygen continues and placed in cold water. After a few minutes the solutions will be cool, and they are then rinsed into Nessler tubes and compared as usual. For high manganese steels (0·75 per cent. Mn and upwards) 0·1 gm. of the sample is taken.

For pig irons and blast-furnace cinders proceed as above until the sample is dissolved, but moisten cinders before adding acid. When solution is effected the suspended matter should be filtered off and the paper washed with the 15 c.c. of silver nitrate solution. Then continue as for steels. Excellent results are shown in comparison with the older peroxide method.

TITRATION METHOD: In place of the above colorimetric comparison, after rapid cooling and before all the persulphate is decomposed (in order to avoid precipitation of manganese as the hydrated oxide), the oxidized solution may be transferred to a small flask and titrated with standard arsenite solution to a pale green. The arsenite solution should be standardized to the same end-point against a steel of known manganese content.

Colorimetric Determination of Small Quantities of Manganese in Water (H. Lührig).[2]

Reagents required.—(*a*) Special distilled water, made by colouring ordinary distilled water with permanganate, distilling, and collecting the distillate after the first 50 c.c. have come over.

---

[1] *C. N.*, 1901, **83**, 76 (Marshall) and **84**, 239 (Walters).

[2] *Chem. Zeit.*, 1914, **38**, 781. The method is apparently based on observations of H. Marshall (see *C. N.*, 1901, **83**, 76).

(*b*) $^{N}/_{100}$ Potassium permanganate, made by dissolving 0·158 gm. of the pure crystals in 500 c.c. of the distilled water (*a*).

1 c.c. = 0·00011 gm. Mn.

METHOD OF PROCEDURE: 100 c.c. of the water to be examined (or more, if necessary, evaporated with a few drops of nitric acid to rather less than 100 c.c.) are mixed with 3 c.c. of concentrated nitric acid and silver nitrate solution in quantity slightly more than sufficient to precipitate the chlorides present, then 3 gm. of ammonium persulphate in strong solution, and the liquid boiled for 5 minutes. If manganese compounds are present, the colour of permanganate is produced, and the cooled liquid is at once nesslerized with a standard permanganate solution made by adding 0·5 or 1 c.c. of permanganate solution (*b*) to 100 c.c. of distilled water (*a*).

EXAMPLE: 250 c.c. of a water were evaporated, after addition of a few drops of nitric acid, to about 95 c.c. and treated as above, using as standard 0·5 c.c. of permanganate solution. 62 c.c. of the standard solution gave the same colour as the prepared sample. Then the amount of Mn in the 250 c.c. taken is

$$\frac{62}{100} \times \cdot0000505 = 0\cdot0000313 \text{ gm. Mn}$$

or 0·0125 part manganese per 100,000.

Results are recorded in which 50 c.c. of water containing 0·044 mgm. Mn gave, as mean values, 0·0498 and 0·0483. Satisfactory results were obtained with tap-water to which from 1 to 10 mgm., Mn were added per litre and treated as above, provided that the water was not allowed to stand too long before the final comparison.

Methods similar to the above are those of Hartwig and Schellbach,[1] and Tillmans and Mildner.[2]

5. Technical Examination of Manganese Ores used for Bleaching Purposes, etc.

The ore, when powdered and dried for analysis, rapidly absorbs moisture on exposing it to the air, and consequently has to be weighed quickly; it is better to keep the powdered and dried sample in a small light stoppered bottle, the weight of which, with its contents and stopper, is accurately known. About 1 or 2 gm., or any other quantity within a trifle, can be emptied into the proper vessel for analysis, and the exact quantity found by reweighing the bottle.

A hardened steel or agate mortar must be used to reduce the mineral to the finest possible powder, so as to ensure its complete and rapid decomposition by the hydrochloric acid.

Considerable discussion has taken place as to the best processes for determining the available oxygen in manganese ores, arising from the fact that many of the ores now on the market contain iron in the ferrous state; and if such ores be analysed by the usual iron method with hydrochloric acid, a portion of the chlorine produced is employed in oxidizing the iron contained in the original ore. Such ores, if examined by Fresenius and Will's method, show, therefore, a higher percentage than by the iron method, since no such consumption of chlorine occurs in the former process. Manufacturers have, therefore, refused to accept certificates of analysis of such ores when based on Fresenius and Will's method. This renders the volumetric processes of more importance, and hence various experiments have been made to ascertain their possible sources of error.

---

[1] *J. S. C. I.*, 1913, **32**, 1125.

[2] *Ibid.*, 1914. **33**, 709.

The results show that the three following methods give very satisfactory results.[1]

6. Direct Analysis by Distillation with Hydrochloric Acid.

This is the quickest and most accurate method of finding the quantity of available oxygen present in any of the ores of manganese or mixtures of them. It also possesses the recommendation that the quantity of chlorine which they liberate is directly expressed in the analysis itself; and, further, gives an estimate of the quantity of hydrochloric acid required for the decomposition of any particular sample of ore, which is a matter of some moment to the manufacturer of bleaching powder.

The apparatus for the operation may be those shown in figs. 35 or 36. For precautions in conducting the distillation see p. 140 *et seq.*

METHOD OF PROCEDURE: In order that the percentage of dioxide shall be directly expressed by the number of c.c of $^N/_{10}$ thiosulphate solution used, 0·4347 gm. of the properly dried and powdered sample is weighed and put into the little flask; solution of potassium iodide in sufficient quantity to absorb all the iodine set free is put into the large tube (if the solution containing $\frac{2}{10}$ eq or 33·2 gm. in the litre be used, about 70 or 80 c.c. will in ordinary cases be sufficient); very strong hydrochloric acid is then poured into the distilling flask, and the operation conducted as on p 141. Each equivalent of iodine liberated represents 1 eq. Cl, also 1 eq. MnO_2.

Instead of using a definite weight, it is well to do as before proposed, namely, to pour about the quantity required out of the weighed sample-bottle into the flask, and find the exact weight afterwards.

Barlow[2] records a good method of separating Mn from the metals of its own group as well as from alkalies and alkaline earths.

For the quantitative determination of Fe and Mn in the same solution as chlorides (other metals except Cr and Al may be present, but are best absent), solution of NH_4Cl is first added, then strong NH_4HO in excess, boil, then add hydrogen peroxide so long as a precipitate is produced, boil for a few minutes, filter, wash with hot water, ignite, and weigh the mixed oxides together as $Fe_2O_3 + Mn_3O_4$.

The oxides are then distilled with HCl, and the amount of iodine found by thiosulphate.

The weight of mixed oxides, minus the Mn_3O_4, gives the weight of Fe_2O_3.

---

[1] See Scherer and Rumpf, *C. N.*, 1869, **20**, 302; also Pattinson, *ibid.*, 1870, **21**, 266; and Paul, **21**, 16.

[2] *C. N.*, 1886, **53**, 41.

Pickering[1] has pointed out that pure manganese oxides, freshly prepared, or the dry oxides in very fine powder, may be rapidly determined without distillation by merely adding them to a large excess of potassium iodide solution in a beaker, running in 2 or 3 c.c. of hydrochloric acid, when the oxides are immediately attacked and decomposed; the liberated iodine is then at once titrated with thiosulphate. Impure oxides, especially those containing ferric oxide, cannot, however, be determined in this way, since the iron would have the same effect as manganic oxide; hence distillation must be resorted to in the case of all such ores, and it is imperative that the strongest hydrochloric acid should be used.

Pickering's modified process is well adapted to the examination of the Weldon mud for its available amount of manganese dioxide.

7. Determination by Oxalic Acid.

The very finely powdered ore is mixed with a known volume of normal oxalic acid solution, sulphuric acid added, and the mixture heated and well shaken, to bring the materials into intimate contact and liberate the CO_2. When the whole of the ore is decomposed, which may be known by the absence of brown or black sediment, the contents of the vessel are made up to a definite volume (say 300 c.c.) and 100 c.c. of the dirty milky fluid well acidified, diluted, and titrated for the excess of oxalic acid by permanganate. If, in consequence of the impurities of the ore, the mixture be brown or reddish coloured, this would, of course, interfere with the indication of the permanganate, and consequently the mixture in this case must be filtered; the 300 c.c. are, therefore, well shaken and poured upon a large filter. When about 100 c.c. have passed through, that quantity can be taken by the pipette and titrated as in the former case.

If the solution be not dilute and freely acid, it will be found that the permanganate produces a dirty brown colour instead of its well-known bright rose-red; if the first few drops of permanganate produce the proper colour immediately they are added, the solution is sufficiently acid and dilute.

If 4·347 gm. of the ore be weighed for analysis, the number of c.c. of normal oxalic acid will give the percentage of dioxide; but as that is rather a large quantity, and takes some time to dissolve and decompose, half the quantity may be taken, when the percentage is obtained by doubling the volume of oxalic acid used.

This process possesses an advantage over the following, inasmuch as there is no fear of false results occurring from the presence of air. The analysis may be broken off at any stage, and resumed at the operator's convenience.

8. Determination by Iron.

Iron wire of 99·8 per cent. purity can readily be obtained; but if perfectly dry and unoxidized ferrous ammonium sulphate be at hand, its use saves time. 1 mol. of this salt (= 392·16), representing 43·47 of MnO_2, consequently, 1 gm. of the latter requires 9·022 gm. of the double salt; or in order that the percentage may be obtained without calculation 1·108 gm. of ore may be weighed and digested in the presence of free sulphuric acid, with 10 gm. of ferrous ammonium sulphate, the whole of which would be required supposing the sample were pure dioxide. The undecomposed ferrous salt remaining at the end of the reaction is determined by permanganate or dichromate; the quantity so found is deducted from the original 10 gm., and if the remainder be multiplied by 10 the percentage of dioxide is arrived at.

---

[1] *J. C. S.*, 1880, 128.

Instead of this plan, which necessitates exact weighing, any convenient quantity may be taken from the tared bottle, as before described, and digested with an excess of ferrous ammonium sulphate, the weight of which is known. After the undecomposed quantity is found by permanganate or dichromate, the remainder is multiplied by the factor 0·111 (or $\frac{1}{9}$), which gives the proportion of dioxide present, whence the percentage may be calculated.

The decomposition of the ore may be made in any of the apparatus used for titrating ferrous iron. The ore is first put into the decomposing flask, then the ferrous salt and water, so as to dissolve the salt to some extent before the sulphuric acid is added. Sulphuric acid should be used in considerable excess, and the flask heated till all the ore is decomposed; the solution is then cooled, diluted, and the whole or part titrated with permanganate or dichromate.

When using $^N/_{10}$ dichromate for the titration, the following plan is convenient: 100 c.c. of $^N/_{10}$ dichromate = 3·922 gm. of ferrous ammonium sulphate (supposing it to be perfectly pure), therefore if 0·4347 gm. of the sample of ore be boiled with 3·922 gm. of the double salt and excess of acid, the number of c.c. of dichromate required deducted from 100 will give the number corresponding to the percentage.

MERCURY.

Hg = 200·6.
1 c.c. $^N/_{10}$ solution = 0·02006 gm. Hg.
= 0·02086 gm. Hg_2O.
= 0·027152 gm. $HgCl_2$.
Ferrous Ammonium Sulphate × 0·5115 = Hg.
" " " × 0·6924 = $HgCl_2$.

1. Precipitation as Mercurous Chloride.

The solution to be titrated must not be warmed, and must contain the metal in the form of protosalt only. $^N/_{10}$ sodium chloride is added in slight excess, filtered, and the precipitate washed with the least possible quantity of water to ensure the removal of all the sodium chloride; to the filtrate a few drops of chromate indicator are added, then pure sodium carbonate till the liquid is of a clear yellow colour, $^N/_{10}$ silver solution is then delivered in till the red colour appears. The quantity of sodium chloride so found is deducted from that originally used, and the difference calculated in the usual way.

2. By Ferrous Oxide and Permanganate (Mohr).

This process is based on the fact that when mercuric chloride (corrosive sublimate) is brought in contact with an alkaline solution of ferrous oxide in excess, the latter is converted into ferric oxide, while the mercuric is reduced to mercurous chloride (calomel). The excess of ferrous oxide is then found by permanganate or dichromate—

$$2HgCl_2 + 2FeCl_2 = Hg_2Cl_2 + Fe_2Cl_6.$$

It is, therefore, advisable in all cases to convert the mercury to be determined into the form of sublimate, by evaporating it to dryness with nitro-hydrochloric acid; this must take place, however, below boiling heat, as vapours of chloride escape with steam at 100° C. (Fresenius).

Nitric acid or free chlorine must be altogether absent during the decomposition with the iron protosalt, otherwise the residual titration will be inexact, and the quantity of the iron salt must be more than sufficient to absorb half the chlorine in the sublimate.

Example: 1 gm. of pure $HgCl_2$ was dissolved in warm water, and 3 gm. of ferrous ammonium sulphate added, then solution of caustic soda till strongly alkaline. The mixture became muddy and dark in colour, and was well shaken for a few minutes, then sodium chloride and sulphuric acid added, continuing the shaking till the colour disappeared and the precipitate of ferric oxide dissolved, leaving the calomel white; it was then diluted to 300 c.c., filtered through a dry filter, and 100 c.c. titrated with $^N/_{10}$ permanganate, of which 13·2 were required—13·2 × 3 = 39·6, which deducted from 76·5 c.c. (the quantity required for 3 gm. ferrous ammonium sulphate), left 36·9 c.c. = 1·447 gm. of undecomposed ferrous salt, which multiplied by the factor 0·6924, gave 1·0005 gm. of sublimate, instead of 1 gm., or the 36·9 c.c. may be multiplied by the $^N/_{10}$ factor for mercuric chloride, which will give 1·002 gm.

3. By Iodine and Thiosulphate (Hempel).

If the mercury exist as a protosalt it is precipitated by sodium chloride, the precipitate well washed and together with its filter pushed through the funnel into a stoppered flask, a sufficient quantity of potassium iodide added, together with $^N/_{10}$ iodine solution (to 1 gm. of calomel about 2·5 gm. of iodide, and 100 c.c. of $^N/_{10}$ iodine), the flask closed, and shaken till the precipitate has dissolved—

$$Hg_2Cl_2 + 6KI + I_2 = 2HgK_2I_4 + 2KCl.$$

The brown solution is then titrated with $^N/_{10}$ thiosulphate till colourless, diluted to a definite volume, and a measured portion titrated with $^N/_{10}$ iodine and starch for the excess of thiosulphate.

1 c.c. $^N/_{10}$ iodine = 0·02006 gm. Hg.

Where the mercurial solution contains nitric acid, or the metal exists as peroxide, it may be converted into protochloride by the reducing action of ferrous sulphate, as in Mohr's method. The solution must contain hydrochloric acid or common salt in sufficient quantity to transform all the mercury into calomel. Ferrous sulphate in solution in quantity equal to at least three times the weight of mercury present is to be added, then caustic soda in excess, the muddy liquid well shaken for a few minutes, then dilute sulphuric acid added in excess, and the mixture stirred till the dark-coloured precipitate has become perfectly white. The calomel so obtained is collected on a filter, well washed, and titrated with $^{N}/_{10}$ iodine and thiosulphate as above.

C. Reichardt[1] has recommended the following method of determining mercury. A weighed quantity of the mercury compound is dissolved and converted into mercury arsenate by boiling with standard arsenious acid and caustic soda in excess. Metallic mercury is precipitated as a black powder. This is filtered and washed, and the amount of unoxidized arsenious acid in the filtrate is found by titration with standard iodine in the usual way.

4. As Mercuric Iodide (Personne).[2]

This process is founded on the fact that if a solution of mercuric chloride be added to one of potassium iodide, in the proportion of 1 equivalent of the former to 4 of the latter, red mercuric iodide is formed, which dissolves to a colourless solution until the balance is overstepped, when the brilliant red colour of the iodide appears as a precipitate, which, even in the smallest quantity, communicates its tint to the liquid. The mercuric solution must always be added to the iodide; a reversal of the process, though giving eventually the same quantitative reaction, is nevertheless much less speedy and trustworthy. The mercurial compounds to be determined by this process must invariably be brought into the form of neutral mercuric chloride.

The standard solutions required are decinormal, made as follows:—

Solution of potassium iodide.—33·2 gm. of pure salt to 1 litre.

1 c.c. = 0·01003 gm. Hg. or 0·013576 gm. $HgCl_2$.

Solution of mercuric chloride.—13·576 gm. of the salt, with about 30 gm. of pure sodium chloride (to assist solution), are dissolved to 1 litre. 1 c.c = 0·01003 gm. Hg.

METHOD OF PROCEDURE: The conversion of various forms of mercury into mercuric chloride is, according to Personne, best effected by heating with caustic soda or potash, and passing chlorine gas into the mixture, which is afterwards boiled to expel excess of chlorine (the mercuric chloride is not volatile at boiling temperature when associated with alkali chloride). The solution is then cooled and diluted to a given volume, placed in a burette, and delivered into a measured volume of the decinormal iodide until the characteristic colour appears. It is preferable to dilute the mercuric solution considerably, and make up to a given measure, say 300 or 500 c.c.; and as a preliminary trial take 20 c.c. or so of iodide solution, and titrate it with the mercuric solution approximately with a graduated pipette; the exact strength may then be found by using a burette of sufficient size.

5. Methods Involving Reduction to the Metallic State.

Iodimetric Method (Rupp).[3] This can be used for mercuric nitrate chloride, or sulphate, as well as for mercuric cyanide.

METHOD OF PROCEDURE: The solution of the mercury salt, containing about 0·2 gm. of mercury in 25 to 50 c.c., is treated with excess of potassium iodide (1 gm.) so that the mercuric iodide that forms is redissolved. The liquid is next rendered alkaline with sodium hydroxide, treated with 2 or 3 c.c. of 40 per cent. formaldehyde solution, diluted with 10 c.c. of water, and vigorously and continuously shaken for one to two minutes. It is then acidified with acetic acid, 25 c.c. of $^{N}/_{10}$ iodine solution added, and the excess of free iodine titrated with $^{N}/_{10}$ sodium thiosulphate solution. The formaldehyde precipitates the mercury, which combines with the iodine to form mercuric iodide, and the excess of iodine is titrated as described. If the mercury be in the form of mercurous salts, it must be brought into the mercuric state before precipitation, by treatment with Br. water, excess of Br. being removed by gentle heating. In the case of mercuric cyanide, sulphuric acid should be used instead of acetic acid for the acidification, so as to decompose any cyanogen iodide that may have been formed.

---

[1] *Z. a. C.*, 1898, **37**, 749.

[2] *Compt. Rend.*, 1863, **56**, 63.

[3] *Ber.*, 1906, **39**, 3702.

Arsenite Method (Feit),[1] modified by Reinthaler.[2]—The mercury must be in the mercuric state.

METHOD OF PROCEDURE: To the mercuric solution, nearly neutralized with caustic soda, $^{N}/_{10}$ sodium arsenite solution is added in quantity more than enough to reduce the whole of the mercury to the metallic state. A current of CO_2 is led into the flask by means of a tube having a bulb blown in it, which serves to stopper the flask loosely and to keep the end of the tube just above the surface of the liquid. The flask and its contents are then heated on the water-bath for ½ hour to 1½ hours, a gentle stream of CO_2 being continued all the time. When the reaction is complete, the precipitate should be a uniform dark grey "flowing" powder. After cooling, the excess of arsenite is titrated directly with $^{N}/_{10}$ iodine solution, without filtration; or excess of iodine may be added and titrated back with arsenite, the solution of mercury by iodine being too slow to affect the result.

6. By Potassium Cyanide (Hannay).

This process is applicable to the determination of almost all the salts of mercury when they occur, or can be separated, in a tolerably pure state. Organic compounds are of no consequence unless they affect the colour of the solution.

The method depends on the fact that free ammonia produces a precipitate or (when the quantity of mercury is very small) an opalescence in mercurial solutions, which is removed by a definite amount of potassium cyanide.

The delicacy of the reaction is interfered with by excessive quantities of ammoniacal salts, or by caustic soda or potash; but this difficulty is lessened by the modifications suggested by Tuson and Neison[3] and Chapman Jones.[4]

I employ a solution of mercuric chloride containing 0·01 gm. of metal per c.c., and a solution of crystallized potassium cyanide made by dissolving 7 gm. to the litre, the exact value of which is found by titrating it against the mercury solution. Strong ammonia diluted to ten times its bulk, and some diluted to fifty or a hundred times its bulk, are convenient.

---

[1] *Z. a. C.*, 1889, **28**, 318.

[2] *Chem. Zeit.*, 1911, **35**, 593.

[3] *J. C. S.*, 1877, **31**, 679.

[4] *Ibid.*, 1892, **61**, 364.

Method of Procedure: If the mercury solution is not fit for titration, the metal is precipitated as sulphide, which, after washing, is washed off the filter and allowed to subside; the clear water is then decanted off, and *aqua regia* added to the moist residue. The precipitate, with the paper it is on, might doubtless be treated direct with *aqua regia*, as Tuson and Neison found that organic matter, so far as they tried it, does not influence the result. To avoid the possibility of volatilizing the mercury salt, the *aqua regia* is allowed to act in the cold. In a few hours, sometimes in far less time, the residue is of a pale yellow colour, and the solution may be diluted and filtered. The solution, or an aliquot part of it, is then coloured distinctly with litmus, treated with successive small quantities of powdered potassium carbonate until alkaline, warming but slightly, and then rendered just acid with dilute hydrochloric acid, with subsequent boiling to remove the CO_2. The mercury is not precipitated at all, unless the CO_2 is boiled out before acidification. After cooling, the dilutest ammonia mentioned above is added, a drop at a time, until the litmus in the solution shows that the excess of acid is very slight, or in just insufficient quantity to produce a permanent precipitate. A quantity of cyanide solution, which is known to be in excess of that required, is added, and, as a guide for the first titration, the ammonia may be added until a slight precipitate is produced, and cyanide until the solution is cleared. Two or three drops (not more) of the 1 in 10 ammonia are introduced, and then more of the mercury solution is added until the permanent turbidity produced matches that obtained by adding 0·1 c.c. of the mercury solution to about the same bulk of water as the test, and containing approximately the same amounts of litmus and free ammonia. Each drop of the mercury solution added produces its maximum turbidity in a few seconds, and it can be seen at a glance, if the flasks are properly placed, whether this turbidity is equal to or less than the standard. In a few seconds more it is quite obvious whether the turbidity is permanent or is growing less. Too much free ammonia causes the precipitate to clot together, and so vitiates the result. The presence of the litmus tends, in my experience, to lessen the error due to the variation in the state of aggregation of the precipitate when too much ammonia has been added. The turbidities so obtained will remain apparently unchanged for many hours. The 0·1 c.c. excess of mercury solution is of course allowed for in the calculation.

Acidimetric Cyanide Method (Rupp)[1].—The solution of the mercuric salt is made neutral by the addition of alkali chloride, followed by phenolphthalein and sufficient alkali to just redden the solution, and then an excess of $^{N}/_{4}$ or $^{N}/_{2}$ potassium cyanide, sufficient to produce an intense red colour, is added, and the excess over that necessary to form mercuric cyanide is titrated with $^{N}/_{1}$ or $^{N}/_{5}$ hydrochloric or sulphuric acid, using methyl orange as indicator. For mercuric chloride, direct titration with potassium cyanide and phenolphthalein is allowable, but in solutions containing much alkali chloride, as obtained with mercuric nitrate and sulphate, the indirect method given above is to be preferred. In order to apply the method to mercuric cyanide, potassium iodide is added, so as to form the compound K_2HgI_4, and liberate potassium cyanide, which is then titrated as above. Mercuric oxide may be dissolved in potassium iodide solution by shaking and the potassium hydroxide formed directly titrated with acid, using methyl orange as indicator.

---

[1] *Chem. Zeit.*, 1908, 32, 1077.

7. Thiocyanate Method.[1]

This may be carried out as for silver salts, see p. 150. It is inapplicable when chlorides, mercurous salts, and nitrous acid are present. It is especially applicable in the presence of nitric acid and heavy metals. Rupp and Nöll[2] have adapted it to the valuation of organic mercury compounds thus:—

METHOD OF PROCEDURE: In order to oxidize the organic matter, 0·3 gm. of the substance is heated in a 150 c.c. flask with 4 gm. of potassium sulphate and 5 c.c. of concentrated sulphuric acid to gentle boiling until quite clear. A reflux condenser 40-50 cm. long is provided to prevent loss of mercury sulphate by volatilization, and this is then rinsed with 5-10 c.c. of concentrated sulphuric acid and removed; 0·1-0·2 gm. of potassium permanganate is now added to ensure the mercury being in the mercuric condition, and the heating continued until the pink colour vanishes. After cooling, the liquid is diluted to about 100 c.c., again allowed to cool, 2 c.c. of 10 per cent. iron alum solution added as indicator, and then titrated with $^{N}/_{10}$ thiocyanate, the flask being frequently rotated.

1 c.c. $_{N}/_{10}$ thiocyanate = 0·01003 gm. Hg

G. S. Jamieson[3] determines the metal in soluble mercuric compounds by precipitating as mercury zinc thiocyanate and titrating the precipitate with potassium iodate solution in the presence of strong hydrochloric acid and chloroform. Conversely, the method determines Zinc (q.v.).

NICKEL.

Ni = 58·68.

1. Cyanometric Method.

THE best method for the determination of this metal volumetrically is that of T. Moore,[4] whose description of the method is as follows:—

"If to an ammoniacal solution of nickel containing AgI in suspension (silver iodide being almost insoluble in weak ammonia) there is added potassium cyanide, the solution will remain turbid so long as all the nickel is not converted into the double cyanide of nickel and potassium, the slightest excess of cyanide being indicated by the clearing up of the liquid, and furthermore, this excess may be exactly determined by adding a solution of silver until the turbidity is reproduced. It is a fortunate circumstance that the complicated side-reactions existing in Parkes's copper assay do not appear to take place with nickel solutions, at least not when the temperature is kept below 20° C. This is fully borne out by the fact that the cyanide may be standardized on either silver or nickel solutions with equal exactness. In practice it has been found best to proceed in the following manner:—

---

[1] *Ber.*, 1902, **35**, 2015.

[2] *Arch. Pharm.*, 1905, **243**, 1-5.

[3] *J. A. C. S.*, 1918, **40**, 1036, and *J. Ind. Eng. Chem.*, 1919, **11**, 296 (abstr.) *Analyst*, 1918, **43**, 338, and 1919, **44**, 213.

[4] *C. N.*, 1895, **72**, 92.

Standard solution of silver nitrate, containing about 3 gm. of silver per litre. The strength of this solution must be accurately known.

Potassium iodide, 10 per cent. solution.

Potassium cyanide, 22 to 25 gm. per litre. This solution must be tested every few days, owing to its liability to change.

Standardizing the Cyanide Solution.—This may be accomplished in two ways; (*a*) on a solution of nickel of known metallic content, or (*b*) on the silver solution.

(*a*) First, accurately establish the relation of the cyanide to the silver solution, by running into a beaker 3 or 4 c.c. of the former; dilute this with about 150 c.c. of water, render slightly alkaline with ammonia, and then add a few drops of the potassium iodide. Now carefully run in the silver solution until a faint permanent opalescence is produced, which is finally caused to disappear by the further addition of a mere trace of cyanide. The respective volumes of the silver and cyanide solutions are then read off, and the equivalent in cyanide of 1 c.c. silver solution calculated. A solution containing a known quantity of nickel is now required. This must have sufficient free acid present to prevent the formation of any precipitate on the subsequent addition of ammonia to alkaline reaction; if this is not so, a little ammonium chloride may be added. A carefully measured quantity of the solution is then taken, containing about 0·1 gm. of nickel, and rendered distinctly alkaline with ammonia, a few drops of iodide added, and the liquid diluted to 150 or 200 c.c. A few drops of the silver solution are now run in, and the solution stirred to produce a uniform turbidity. The solution is now ready to be titrated with the cyanide, which is added slowly and with constant stirring until the precipitate wholly disappears; a few extra drops are added, after which the beaker is placed under the silver nitrate burette, and this solution gently dropped in until a faint permanent turbidity is again visible; this is now finally caused to dissolve by the mere fraction of a drop of the cyanide. A correction must now be applied for the excess of the cyanide added, by noting the amount of silver employed, and working out its value in cyanide from the data already found; this excess must then be deducted, the corrected number of c.c. being then noted as equivalent to the amount of nickel employed.

(*b*) Having determined the relative value of the cyanide to the silver solution, and knowing accurately the metallic content of the latter, then Ag × 0·272 gives the nickel equivalent. This method is quite as accurate as the direct titration.

A modification of the above process, wherein one burette only is necessary, has been found very convenient, and has given most excellent results. It is as follows:—

When a solution of potassium cyanide, containing a small quantity of silver cyanide dissolved in it, is added to an ammoniacal solution of nickel containing potassium iodide, it is seen that silver iodide is precipitated, and the turbidity thus caused in the solution continues to increase up to the point where the formation of the nickel-potassium cyanide is complete; any further addition after this stage is reached will produce a clearing up of the liquid, until, at last, the addition of a single drop causes the precipitate to vanish. This final disappearance is most distinct, and leaves no room for doubt. Such a solution may be prepared by dissolving 20 to 25 gm. of potassium cyanide in a litre of water, adding to this about 0·25 gm. silver nitrate, previously dissolved in a little water. For large quantities of nickel the quantity of silver may advantageously be diminished, and *vice versâ*. The value of the cyanide is best ascertained, in the manner already described, on a nickel solution.

Small quantities of cobalt do not seriously affect the results, but it must be remembered that it will be reckoned with the nickel; its presence is at once detected by the darkening of the solution. Manganese[1] or copper, when present, render the process valueless, so also does zinc; the latter, however, in alkali pyrophosphate solution exercises no influence. In the presence of alumina, magnesia, or ferric oxide, citric acid, tartaric acid, or pyrophosphate of soda may be employed to keep them in solution. The action of iron is somewhat deceptive, as the solution, once cleared up, often becomes turbid again on standing for a minute: should this occur, a further addition of cyanide must be made until the liquid is rendered perfectly clear. The temperature of the solution should not much exceed 20° C.: above this the results become irregular. The amount of free ammonia has also a disturbing influence; a large excess hinders or entirely prevents the reaction; the liquid should, therefore, be only slightly, but very distinctly, alkaline. A word of caution must be given regarding the potassium cyanide, as many of the reputed pure samples are very far from being so. The most harmful impurity is, however, sulphur, as it gives rise to a darkening of the solution, owing to the formation of the less readily soluble silver sulphide; to get rid of the sulphur impurity it is necessary to thoroughly agitate the cyanide liquor with oxide of lead, or, what is far preferable, oxide of bismuth.

As regards the exactness of the methods, it may be said that, after a prolonged experience, extending over many thousands of determinations, they have been found to be more accurate and reliable than either the electrolytic or gravimetric methods, and when time is a consideration the superiority is still more pronounced. The employment of organic acids or sodium pyrophosphate in the case when iron, zinc, etc., are present, allows the operator to dispense with the tedious separation which their presence otherwise entails; and this is a matter of considerable importance in the assay of nickel mattes or German silver."

All analysts will agree with Brearley and Ibbotson's[2] statement that "the cyanometric estimation of nickel is one of the most stable and exact processes to be found in the literature of metallurgical analysis". As an elegant process of volumetric analysis it ranks second only to Volhard's method of determining silver.

Note on the Influence of Manganese.—The statement of Moore, quoted above, that the presence of manganese renders the method valueless is not true, at any rate in respect of the amounts usually present in steel, in the analysis of which for nickel by this method manganese is commonly ignored. Brearley and Ibbotson (loc. cit.) say "the harmlessness of manganese should be emphasized," and they justify this opinion by citing the results of titrating 0·1 gm. of nickel in the presence of (1) 0·05 gm., and (2) 0·1 gm. of manganese. The nickel found was (1) 0·0999 gm., and (2) 0·1002 gm.

---

[1] See Note on the influence of manganese, *infra*.

[2] *Analysis of Steel Works Materials*, 1902.

Nickel-plating Solutions.—These contain, as a rule, only nickel sulphate and ammonia, and the nickel can be determined with a simple solution of potassium cyanide previously standardized on pure nickel ammonium sulphate. The nickel solution to be tested should be fairly concentrated and rendered feebly alkaline with ammonia. If there is iron present some ammonium tartrate should be added to prevent the precipitation of it by the ammonia. The cyanide is used in small quantities with constant shaking until a drop produces a clear yellowish solution. Copper, zinc, and cobalt must not be present.

Jamieson[1] has published the following modification of the above process for the determination of **nickel in steel**:—

Dissolve 0·5 gm. of borings in 10 c.c. dilute nitric acid (1 : 1) in a 150 c.c. flask, according to the directions given for the ferrocyanide method.[2] If the metal contains more than 0·5 per cent. of manganese, remove it according to the same directions. Add to the nitric acid solution 2-3 gm. citric acid and 2 gm. anhydrous sodium pyrophosphate, then add ammonia slowly with stirring until the precipitate at first formed just dissolves and the solution acquires a very faint odour of ammonia. If too much ammonia has been used, it must be nearly neutralized by the careful addition of nitric acid. Dilute to about 150 c.c. and cool to a temperature below 20°, add a few drops of a 10 per cent. solution of KI and enough $^{N}/_{10}$ silver nitrate solution—the volume of which must be noted—to produce a distinct turbidity. Then run in KCy solution very slowly with stirring until the turbidity just disappears, and the solution lightens to a golden-yellow colour. The solution should remain bright for 5 minutes, otherwise the titration is incomplete. Sometimes it happens that the turbidity disappears when only one-third to one-half of the required amount of cyanide has been used, but in this case on the addition of a drop or two of silver nitrate, or on waiting a moment, the turbidity reappears. The end-point is best observed when the beaker is placed on a white paper having an elliptical hole in it under which is placed a black glazed paper for contrast. In making the calculation the proper deduction for the silver nitrate used should be made.

The potassium cyanide solution should be standardized by means of the $^{N}/_{10}$ silver nitrate. To do this, pipette 20 c.c. into a beaker, dilute to about 150 c.c. with cold water, add ammonia until the odour is distinct but slight, add a few drops of 10 per cent. KI solution, run in silver nitrate until a distinct turbidity is produced, and then finish by slowly adding the cyanide solution until the turbidity just disappears. The theoretical amount of nickel per c.c. of $^{N}/_{10}$ solution is 0·002934 gm., but instead of using this value it is perhaps preferable to standardize the solution with a steel of known content of nickel.

---

[1] *C. N.*, 1910, **102**, 51.

[2] See 2, *infra*.

The titration in a tartaric or citric acid solution of a steel has the drawbacks that it is difficult to observe the exact point when the final turbidity is formed, and that the excess of ammonia added is not controlled. E. H. Hall[1] obviates the first drawback by transferring the solution, before complete neutralization, to a measuring cylinder, which is supported over a mirror adjusted to reflect light upwards through the column of liquid. He overcomes the other difficulty by taking advantage of the fact that silver chloride is soluble in ammonia, and that as soon as free ammonia is present any cloudiness due to the chloride will disappear.

The Rapid Determination of Nickel in the Presence of Chromium, Iron, and Manganese (C. M. Johnson's modification of T. Moore's Method).[2]

Solutions required.—(1) Potassium cyanide containing 4·487 gm. of the pure salt to the litre, 5 gm. of potassium hydroxide being also added (this addition causes the solution to retain its strength permanently). 1 c.c. = (about) 0·001 gm. Ni. (2) Silver nitrate containing 2·925 gm. of the salt in 500 c.c.

METHOD OF PROCEDURE FOR PLAIN NICKEL STEELS: Dissolve 1 gm. of steel drillings in a 150 c.c. beaker with 20 c.c. hydrochloric acid (1 : 1). When action has ceased, add 10 c.c. of nitric acid (1·2). Reduce the volume of the solution to about 15 c.c., keeping the beaker covered during the boiling. Remove the beaker from the source of heat and pour into it 8 c c. of concentrated H_2SO_4 diluted with 24 c.c. of water. Transfer the contents of the beaker to a 600 c.c. beaker containing 12 gm. of powdered citric acid, and stir until the citric acid is dissolved. Add ammonia solution (1 : 1) cautiously until the solution becomes faintly but distinctly alkaline (a large excess of ammonia causes low results). Cool the solution, which should be about 300 c.c. and of a brownish shade, and when cold add 2 c.c. of a 20 per cent. potassium iodide solution. Now add from a burette silver nitrate solution (2) to produce with the iodide a white turbidity, then run in from a burette standard potassium cyanide (1) with constant stirring until the cloud of silver iodide just disappears (on being converted into silver cyanide).

(i) $Ni(NO_3)_2 + 4KCN = Ni(CN)_2 . KCN + 2KNO_3$.

(ii) $AgNO_3 + 2KCN = AgCN . KCN + KNO_3$.

In order to standardize the solutions, weigh 0·2 gm. and 0·25 gm. of pure nickel ammonium sulphate into 150 c.c. beakers, together with 1 gm. of plain carbon steel drillings. This mixture is then put through all the foregoing manipulations and titrated with the cyanide solution to be standardized, the number of c.c. of the silver nitrate and potassium cyanide solutions used in each case being noted. An excess of 10 c.c. of the cyanide is now added and in turn titrated with the silver nitrate solution until a distinct cloud of silver iodide is produced. This second titration gives the relation between the silver and the cyanide solutions. An example will make the matter clear.

---

[1] *J. S. C. I.*, 1920, **39**, 253T.

[2] *Rapid Methods for the Analysis of Special Steels, etc.*, by C. M. Johnson, 3rd edition, 1920, p. 220 *et seq.*

In one case 1·7 c.c. of the silver nitrate solution was required to produce a slight turbidity, and 35 c.c. of the cyanide solution were required to render the liquid clear. An excess of 9·8 c.c. of cyanide was then added and exactly 10·1 c.c. of the silver solution were needed to reproduce a slight turbidity. Therefore, 1 c.c. of silver nitrate equals 9·8/10·1 = 0·97 c.c. of cyanide solution, and 1·7 × 0·97 or 1·65 c.c. must be deducted from the c.c. of cyanide used instead of 1·7 c.c. Hence 35·0 - 1·65 = 33·35 c.c. of cyanide solution combined with the nickel in this steel. As this cyanide solution, when standardized, gave 1 c.c. = 0·00103 gm. nickel, the percentage of nickel present equals 33·35 × 0·00103 × 100 = 3·435.

In the case of **Chromium-nickel steels** proceed exactly as described above, except that 24 gm. of citric acid per gm. of steel are used. This proportion of citric acid suffices to render the end-point quite as easy to see as in ordinary nickel steels.

2. Determination of Nickel and Cobalt by Potassium Ferrocyanide.

Solution required.—Standard potassium ferrocyanide solution, 20 gm. per litre (1 c.c. = about 0·003 gm. Ni or Co).

This method is referred to by Cantoni and Rosenstein[1] and is described in detail by Jamieson[2]; it is applicable for the determination of nickel and cobalt, but cannot be used in the presence of copper, zinc and manganese. The following procedure is recommended by Jamieson for standardizing the ferro-cyanide solution, a similar course being pursued with the nickel or cobalt solution to be tested :—

A solution of nickel or cobalt is made from a pure salt and of known strength. Three equal portions, each containing about 0·1 gm. of the metal, are measured into beakers. 10 c.c. of a 10 per cent. solution of ferric chloride and 2 to 3 gm. of citric acid are added to each, and then ammonia with stirring until the liquid has a faint smell of the reagent—a large excess being carefully avoided. The solutions are then diluted to about 100 c.c. with hot water and brought to a temperature of 63 to 75° C. The ferrocyanide is then run in *slowly* from a burette with constant stirring. A drop of the solution is from time to time transferred to a paraffined white plate and acidified with a drop of dilute acetic acid. The titration is finished when a greenish colour appears after 5 minutes' standing. The first portion is used to get an approximate result; the exact end-point being determined in the other two.

Determination of Nickel in Steel.—Dissolve 1 gm. of the borings in 10 to 15 c.c. dilute nitric acid (1 : 1) in a 150 c.c. flask covered with an inverted crucible cover. When the first violent action is over, remove cover, and boil gently with constant motion over a Bunsen flame till the steel is dissolved, adding, if necessary, a few drops of strong HCl or a crystal of $KClO_3$ to complete solution. Now add 10 c.c. of conc. HNO_3, heat to boiling again, and add 0·5 gm. $KClO_3$. Boil off the chlorine, then add another 0·5 gm. of chlorate, and boil for two minutes. Allow the flask to cool a little and filter off the MnO_2 on a Gooch crucible, and wash with as small a quantity of cold water as possible. Then proceed according to the method described above. As the presence of a large amount of iron somewhat retards the appearance of the end-reaction, the ferrocyanide solution used should be standardized in the presence of about the same amount of iron as is contained in 1 gm. of steel. The results are accurate.

---

[1] *Analyst*, 1908, **33**, 107.

[2] *C. N.*, 1910, **102**, 51.

3. Determination of Cobalt and Nickel (Rupp and Pfennig).[1]

Cobalt.—The following method is based on the formation of a double cyanide, which is decomposed by excess of cobalt ions with formation of insoluble cobalt cyanide. 1 atom of cobalt was found to correspond to 5 molecules of KCN.

The cobalt solution, which must be neutral and contain between 0·02 and 0·75 per cent. of cobalt, is run from a burette into a measured volume (5 to 25 c.c.) of $^N/_2$ potassium cyanide (undiluted) until a permanent brownish turbidity is produced.

1 c.c. $^N/_2$ KCN = 0·0059 gm. cobalt.

$^N/_2$ KCN prepared from pure cyanide can be standardized by $^N/_4$ or $^N/_2$ HCl or H_2SO_4 using methyl orange as indicator.

Nickel.—Exactly the same procedure is followed with regard to nickel. The neutral solution, diluted to contain 0·4 to 1·0 per cent. nickel, is run into 10 c.c. of $^N/_2$ cyanide until a **permanent** turbidity is seen. Before commencing the titration 5 to 20 drops of 10 per cent. ammonia should be added to the cyanide solution, as an increased sharpness of the end-reaction is thus secured: the addition of more than 5 c.c. however, leads to very erroneous results.

1 c.c. $^N/_2$ KCN = 0·007335 gm. Ni.

The method may also be carried out in the reverse way—for nickel, but not for cobalt—as follows: To the (neutral) nickel solution add 10 drops of a 1 per cent. phenolphthalein solution, then run in $^N/_2$ cyanide from a burette until the precipitate formed is redissolved and a red tint obtained, showing the formation of the double cyanide. The addition of one drop more causes the formation of the usual red colour.

Another modification, also applicable to nickel only, is as follows: To the neutral nickel solution is added a measured quantity of cyanide, more than sufficient to form the double cyanide, and the excess determined by titration with $^N/_2$ HCl or H_2SO_4, using methyl orange as indicator.

---

[1] *Chem. Zeit.*, 1910, **34**, 322, and *J. S. C. I.*, 1910, **29**, 518.

NITROGEN AS NITRATES AND NITRITES.

Nitric Anhydride.

$N_2O_5 = 108·02.$

Nitrous Anhydride.

$N_2O_3 = 76·02.$

Normal acid × 0·0540 = N_2O_5
Ditto × 0·1011 = KNO_3
Metallic iron × 0·3761 = HNO_3
Ditto × 0·6035 = KNO_3
Ditto × 0·3224 = N_2O_5

THE accurate determination of nitric acid in combination presents great difficulties, and can only be made by indirect means; the methods here given are sufficient for most purposes. Very few of them can be said to be simple, but it is to be feared that no simple process can ever be obtained for the determination of nitric acid in many of its combinations.

1. Determination by conversion into Ammonia (Schulze and Vernon Harcourt).

This method is based on the fact that when a nitrate is heated with a strong alkaline solution, and zinc added, ammonia is evolved; when zinc alone is used, however, the quantity of ammonia liberated is not a constant measure of the nitric acid present. Vernon Harcourt and Siewart[1] appear to have arrived independently at the result that by using a mixture of zinc and iron the reaction became quantitative.

A convenient form of apparatus is shown in fig. 43.

METHOD OF PROCEDURE: The distilling flask holds about 200 c c. and is closely connected by a bent tube with another smaller flask, in such a manner that both may be placed obliquely upon a sand-bath, the bulb of the smaller flask coming just under the neck of the larger. The oblique direction prevents the spurting of the boiling liquids from entering the exit tubes, but as a further precaution these latter are in both flasks turned into the form of a hook; from the second flask, which must be somewhat wide in the mouth, a long tube passes through a Liebig's condenser (which may be made of wide glass tube) into an ordinary tubulated receiver, containing normal sulphuric acid coloured with an indicator. The end of the distilling tube reaches to about the middle of the receiver, through the tubulure of which Harcourt passes a bulb apparatus of peculiar form, containing also coloured normal acid; instead of this latter, however, a chloride of calcium tube, filled with broken glass, and moistened with acid, will answer the purpose. The distilling tube should be cut at about two inches from the cork of the second flask, and connected by means of a well-fitting vulcanized tube;

---

[1] *J. C. S.*, 1862, **15**, 381; *An. Chem. u. Phar.*, **125**, 293.

by this means water may be passed through the tube when the distillation is over so as to remove any traces of ammonia which may have been retained on its sides. All the corks of the apparatus should be soaked in hot paraffin, so as to fill up the pores.

All being ready, about 50 gm. of finely granulated zinc (best made by pouring molten zinc into a warm iron mortar while the pestle is rapidly being rubbed round) are put into the larger flask with about half the quantity of clean iron filings which have been ignited in a covered crucible (fresh iron and zinc should be used for each analysis); the weighed nitrate is then introduced, either in solution, or with water in sufficient quantity to dissolve it, strong solution of caustic potash added, and the flask immediately connected with the apparatus, and placed on a small sand-bath, which can be heated by a gas-burner, a little water being previously put into the second flask. Convenient proportions of material are ½ gm. nitre, and about 25 c.c. each of water and solution of potash of specific gravity 1·3. The mixture should be allowed to remain at ordinary temperature for about an hour (Eder).

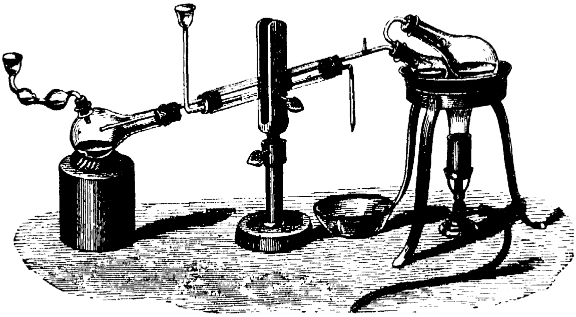

FIG. 43.

Heat is now applied to that part of the sand-bath immediately beneath the larger flask, and the mixture is gradually raised to the boiling point. When distillation has actually commenced, the water in the second flask is made to boil gently; by this arrangement the fluid is twice distilled, and any traces of fixed alkali which may have escaped the first are sure to be retained in the second flask. The distillation with the quantities above-named will occupy about an hour and a half, and is completed when hydrogen is pretty freely liberated as the potash becomes concentrated. The lamp is then removed, and the whole allowed to cool, the distilling tube rinsed into the receiver, also the tube containing broken glass; the contents of the receiver are then titrated with $^{N}/_{10}$ caustic potash or soda as usual.

Eder recommends that an ordinary retort, with its neck set upwards, should be used instead of the flask for holding the nitrate, and that an aspirator should be attached to the exit tube, so that a current of air may be drawn through during and after the distillation.

Chlorides and sulphates do not interfere with the process.

This method is simplified in some agricultural experiment stations for the analysis of sodium and potassium nitrates.

METHOD OF PROCEDURE : 0·5 gm. of the nitrate is dissolved in about 50 c.c. of water in a convenient flask fitted with a bulb distilling tube such as is shown in fig. 27. To the liquid is added about 5 gm. each of zinc dust and iron filings, then 80 c.c. of sodium hydrate solution (sp. gr. 1·3). The mixture is allowed to stand at ordinary temperature for an hour, when the distillation is commenced by heating up carefully and distilling until at least 100 c.c. are received into standard acid through a condenser, as in the Kjeldahl process.

Schmitt has suggested a further modification of this method, technically useful for mixed manures.

METHOD OF PROCEDURE : About 1 gm. of the substance in which the nitrate is to be determined is dissolved in water, 5 c.c. of glacial acetic acid and 3 gm. of a mixture of equal weights of finely powdered iron and zinc added, and the flask gently heated for 10 or 15 minutes. When cooled, 25 c.c. of sulphuric acid are cautiously added and a little solid paraffin to prevent frothing. The flask is then gently heated to drive off the acetic acid, and the residue boiled as in the Kjeldahl method until colourless. Caustic soda in excess is then added and the distillation commenced in the usual way, receiving the distillate into standard acid.

2. By Oxidation of Ferrous Salts (Pelouze).

(Not available in the presence of Organic Matter.)

This is the oldest method for the quantitative determination of combined nitric acid. The following reaction takes place :—

$$3FeCl_2 + HNO_3 + 3HCl = 3FeCl_3 + NO + 2H_2O$$

An excess of ferrous chloride having been taken, that remaining after oxidation has been completed is determined either with standard dichromate or permanganate. The equation shows that 3 × 55·84 = 167·52 parts of ferrous iron oxidized correspond to 63·018 parts of HNO_3, or iron oxidized × 0·3762 = HNO_3.

This method, though theoretically perfect, is in practice liable to serious errors, owing to the readiness with which a solution of a ferrous salt absorbs oxygen from the atmosphere. On this account accurate results are only obtained by conducting hydrogen or carbon dioxide through the apparatus while the boiling is being carried on. This modification has been adopted by Fresenius with very satisfactory results.

The boiling vessel may consist of a small tubulated retort, supported in such a manner that its neck inclines upward; a cork is fitted into the tubulure, and through it is passed a small tube connected with a vessel for generating either carbonic acid or hydrogen. If a weighed quantity of pure metallic iron is used for preparing the solution, the washed carbonic acid or hydrogen should be passed through the apparatus while it is being dissolved; the solution so obtained, or one of double sulphate of iron and ammonia of known strength, being already in the retort, the nitrate is carefully introduced, and the mixture heated gently by a small lamp, or by the water bath, for 10 minutes or so, then boiled until the dark-red colour of the liquid disappears and gives place to the brownish-yellow of ferric compounds. The retort is then allowed to cool, the current of carbonic acid or hydrogen still being kept up, then the liquid diluted freely, and titrated with $^N/_{10}$ permanganate.

Owing to the irregularities attending the use of permanganate with hydrochloric acid, it is preferable, in case this acid has been used, to dilute the solution less, and titrate with dichromate. Two grams of pure iron, or its equivalent in double iron salt, 0·5 gm. of saltpetre, and about 60 c.c. of strong hydrochloric acid, are convenient proportions for the analysis.

Eder[1] has modified Fresenius's improvements as follows:—

1·5 gm. of very thin iron wire is dissolved in 30 to 40 c.c. of pure fuming hydrochloric acid, placed in a retort of about 200 c.c. capacity; the neck of the retort points upwards, at a moderately acute angle, and is connected with a U-tube, which contains water. Solution of the iron is hastened by applying a small flame to the retort. Throughout the entire process a stream of CO_2 is passed through the apparatus. When the iron is all dissolved the solution is allowed to cool, the stream of CO_2 being maintained; the weighed quantity of nitrate contained in a small glass tube (equal to about 0·2 gm. HNO_3) is then quickly passed into the retort through the neck; the heating is continued under the same conditions as before, until the liquid assumes the colour of ferric chloride. The whole is allowed to cool in a stream of CO_2; water is added in quantity, and the unoxidized iron is determined by titration with permanganate. The results are exceedingly good.

If the CO_2 be generated in a flask, with a tube passing downwards for the reception of the acid, air always finds its way into the retort, and the results are unsatisfactory. Eder recommends the use of Kipp's CO_2 apparatus. By carrying out the operation exactly as is now to be described, he has obtained very good results with ferrous sulphate in place of chloride.

The same apparatus is employed; the tube through which CO_2 enters the retort passes to the bottom of the liquid therein, and the lower extremity of this tube is drawn out to a fine point. The bubbles of CO_2 are thus reduced in size, and the whole of the nitric acid is removed from the liquid by the passage of these bubbles. The iron wire is dissolved in excess of dilute sulphuric acid (strength 1 : 3 or 1 : 4). When the liquid in the retort has become cold, a small tube containing the nitrate is quickly passed, by means of a piece of platinum wire attached to it, through the tubulus of the retort, and the cork is replaced before the tube has touched the liquid; CO_2 is again passed through the apparatus for some time, after which, by slightly loosening the cork, the tube containing the nitrate is allowed to fall into the liquid. The whole is allowed to remain at the ordinary temperature for about an hour—this is essential—after which time the contents of the retort are heated to boiling, CO_2 being passed continuously into the retort, and the boiling continued till the liquid assumes the light yellow colour of ferric sulphate.

---

[1] *Z. a. c.*, 1877, **16**, 267.

After cooling, water is added (this may be omitted with dichromate), and the unoxidized iron is determined by permanganate.

Eder also describes a slight modification of this process, allowing of the use of a flask in place of the retort, and of ammonium ferrous sulphate in place of iron wire. Although the titration with permanganate is more trustworthy when sulphuric acid is employed than when hydrochloric acid is used, he nevertheless thinks that the use of ferrous chloride is generally to be recommended in preference to that of ferrous sulphate. When the chloride is employed, no special concentration of acid is necessary; the nitric oxide is more readily expelled from the liquid, and the process is finished in a shorter time. Some manganese sulphate should, however, be used to prevent the disturbing effect of HCl when permanganate is used for titration.

The final point in the titration with permanganate, when the sulphate is employed, is rendered more easy of determination by adding a little potassium sulphate to the liquid.

Direct Titration of the Resulting Ferric Salt by Stannous Chloride.—Fresenius has adopted the use of stannous chloride for titrating the ferric salt with very good results.

The following plan of procedure is recommended by the same authority.

A solution of ferrous sulphate is prepared by dissolving 100 gm. of the crystals in 500 c.c. of hydrochloric acid of sp. gr. 1·10; when used for the analysis, the small proportion of ferric oxide invariably present in it is found by titrating with stannous chloride. The nitrate being weighed or measured, is brought together with 50 c.c. (more or less, according to the quantity of nitrate) of the iron solution into a long-necked flask, through the cork of which two glass tubes are passed, one connected with a CO_2 apparatus, and reaching to the middle of the flask, the other simply an outlet for the passage of the gas. When the gas has driven out all the air, the flask is at first gently heated, and eventually boiled, to dispel all the nitric oxide. The CO_2 tube is then rinsed into the flask, and the liquid, while still boiling hot, titrated for ferric chloride, as on p. 133.

The liquid must, however, be allowed to cool before titrating with iodine for the excess of stannous chloride. While cooling, the stream of CO_2 should still be continued. The quantity of iron changed into peroxide, multiplied by the factor 0·3761, will give the amount of nitric acid (HNO_3).

EXAMPLE: (1) A solution of stannous chloride was used for titrating 10 c.c. of solution of pure ferric chloride containing 0·2151 gm. Fe, 25·65 c.c. of tin solution were required, therefore that quantity was equal to 0·0809 gm. of HNO_3, or 0·06932 gm. of N_2O_5.

(2) 50 c.c. of acid ferrous sulphate were titrated with tin solution for ferric oxide, and 0·25 c.c. was required.

(3) 1 c.c. tin solution = 3·3 c.c. iodine solution.

(4) 0·2177 gm. of pure nitre was boiled, as described, with 50 c.c. of the acid ferrous sulphate, and required 45·05 c.c. tin solution, and 4·7 c.c. iodine:—

4·7 c.c. iodine solution $= 1{\cdot}42$ c.c. $SnCl_2$
The peroxide in the protosulphate solution $= 0{\cdot}25$ c.c.
$1{\cdot}67$

$$45{\cdot}05 - 1{\cdot}67 = 43{\cdot}38$$
$$\therefore 25{\cdot}65 : 43{\cdot}38 = 0{\cdot}06934 \,.\, x$$
$$x = 0{\cdot}1173\ N_2O_5$$

instead of 0·1163, or 53·69 per cent. instead of 53·42. A mean of this and three other determinations, using varying proportions of tin and iron solutions, gave exactly 53·42 per cent. In the case of pure materials, therefore, the process is entirely satisfactory.

The above process is slightly modified by Eder. About 10 gm. of ferrous ammonium sulphate are dissolved in a flask in about 50 c.c. of hydrochloric acid (sp. gr. 1·07) in a stream of CO_2. The tube through which the CO_2 enters is drawn to a point; an exit tube, somewhat trumpet-shaped, to admit of any liquid that may spurt finding its way back into the flask, passes downwards into water. After solution of the double salt, the nitrate is dropped in with the precautions already detailed, and the liquid is boiled until the nitric oxide is all expelled. The hot liquid is diluted with twice its own volume of water, excess of stannous chloride solution run in, the whole allowed to cool in a stream of CO_2, and the excess of tin determined by means of standard iodine.

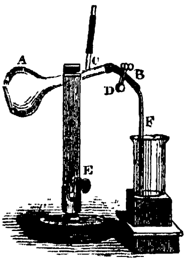

Fig. 44.

Holland's Modification of the Pelouze Process.—The arrangement of apparatus shown in fig. 44 obviates the use of an atmosphere of H or CO_2. A is a long-necked assay-flask drawn off at B, so as to form a shoulder, over which is passed a piece of stout india-rubber tube, D, about 6 centimetres long, the other end terminating in a glass tube, F, drawn off so as to leave only a small orifice. On the rubber connector D is placed a screw clamp. At C, a distance of 3 centimetres from the shoulder, is cemented with a blow-pipe a piece of glass tube about 2 centimetres long, surmounted by one of stout rubber tube, rather more than twice that length. The rubber tubes must be securely attached to the glass by binding with wire.

Method of Procedure: A small funnel is inserted into the rubber tube at C, the clamp at D being for the time open; after the introduction of the solution, followed by a little water which washes all into the flask, the funnel is removed, and the flask supported, by means of the wooden clamp, in the inclined position it occupies in the figure. The contents are now made to boil so as to expel all air and reduce the volume of the fluid to about 4 or 5 c.c. When this point is reached a piece of glass rod is inserted into the elastic tube at C, which causes the water vapour to escape through F.

Into the small beaker is put about 50 c.c. of a previously boiled solution of ferrous sulphate in hydrochloric acid (the amount of iron already existing in the ferric state must be known).

The boiling is still continued for a moment to ensure perfect expulsion of air from F, the lamp is then removed, and the rubber connector slightly compressed with the first finger and thumb of the left hand. As the flask cools the solution of iron is drawn into it: when the whole has nearly receded the rubber tube is tightly compressed with the fingers, whilst the sides of the beaker are washed with a jet of boiled water, which is also allowed to pass into the flask. The washing may be repeated, taking care not to dilute more than is necessary or to admit air. Whilst F is still full of water, the rubber connector previously compressed with the fingers is now securely closed with the clamp, the screw of which is worked with the right hand. Provided the clamp is a good one, F will remain full of water during the subsequent digestion.

After heating in a water bath at 100° for half an hour, the flask is removed from the water bath and cautiously heated with a small flame, the fingers at the same time resting on the rubber connector at the point nearest the shoulder; as soon as the tube is felt to expand, owing to the pressure from within, the lamp is removed and the screw clamp released, the fingers maintaining a secure hold of the tube, the gas-flame is again replaced, and when the pressure on the tube is again felt, this latter is released altogether, thus admitting of the escape of the nitric oxide, through F, which should be below the surface of water in the beaker whilst these manipulations are performed. The contents of the flask are now boiled until the nitric oxide is entirely expelled, and the solution of iron shows only the brown colour of the perchloride. At the completion of the operation, the beaker is first removed, and then the lamp.

It now only remains to transfer the ferric solution to a suitable vessel and determine the perchloride with stannous chloride as above.

A mean of six experiments for the percentage determination of N_2O_5 in pure nitre gave 53·53 per cent. instead of 53·42. The process is easy of execution, and gives satisfactory technical results. The point chiefly requiring attention is that the apparatus should be air-tight, which is secured by the use of good rubber tubes and clamp.

3. Schlosing's Method (Available in the Presence of Organic Matter).

The solution of nitrate is boiled in a flask till all air is expelled, then an acid solution of ferrous chloride drawn in, the mixture boiled, and the nitric oxide gas collected over mercury in a balloon filled with mercury and milk of lime; the gas is then brought, without loss, in contact with oxygen and water, so as to convert it again into nitric acid, then titrated with $^N/_{10}$ alkali as usual.

This method was devised by Schlösing for the determination of nitric acid in tobacco, and is especially suitable for that and similar purposes, where the presence of organic matter would interfere with the direct titration of the iron solution. Where the quantity of nitric acid is not below 0·15 gm. the process is fairly accurate, but needs a special and rather complicated arrangement of apparatus, the description of which may be found in Fresenius's *Quant. Anal.*, sixth edition.

An arrangement of apparatus, dispensing with the use of mercury, has been devised by Wildt and Scheibe,[1] which simplifies the method and gives accurate results with not less than 0·25 gm. N_2O_5. With smaller quantities the results are too low. Fig. 45 shows the apparatus used.

---

[1] *Z. a. C.*, **23**, 151.

A is a conical flask of 250 c.c. capacity, containing the solution to be analysed. B is a round-bottomed flask of 250 to 300 c.c. capacity, half filled with caustic soda, to absorb any HCl which might be carried over from A. C is a conical flask of 750 c.c. capacity, containing a little water to absorb the nitric acid. D is a tube containing water to collect any nitric acid not absorbed by the water in C. The tube *d* is bent, as shown in the diagram, and drawn out to a point, to diminish the size of the bubbles. The tube *e* is wide, and cut obliquely to prevent water collecting and passing into C.

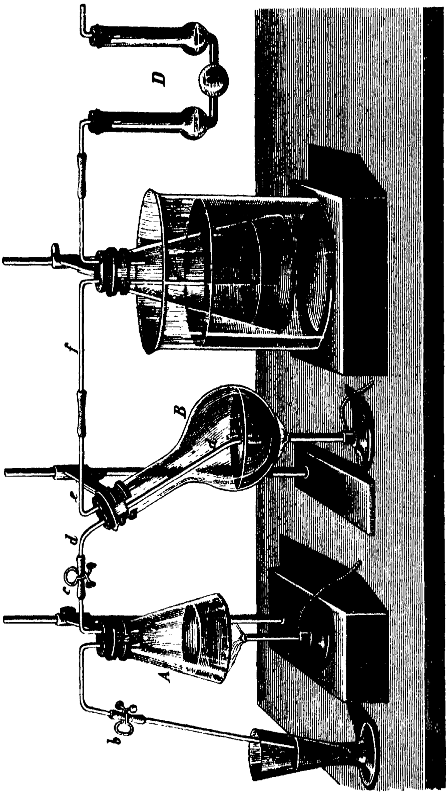

Fig. 45.

Method of Procedure: The clip *b* is closed and *c* opened, and the tube *e* disconnected from *f*. The solutions in A and B are then boiled for 20 minutes to remove all oxygen. The tubes *e* and *f* are again connected, the clip *c* is closed, the flame under B increased to prevent the liquid in C from being drawn back, and the clip *b* is opened. As soon as steam issues from the tube *a*, it is dipped into a conical glass containing 50 c.c. of ferrous chloride prepared according to Schlösing's directions, and the flame under A is removed, when the ferrous chloride enters the flask. The clip *b* is regulated with the finger and thumb, so as to prevent the entry of air into the flask. The conical vessel is rinsed 2 or 3 times with water, and this is allowed to enter the flask, and the clip *b* is then closed, and the vessel A heated. The liquid in A turns brown in a short time, and nitric oxide is evolved. The clip *c* is opened slightly from time to time until the pressure is high enough, when it is opened entirely. The flames must be so regulated that a slow current of gas bubbles through the water in C. The hydrochloric acid is removed by the caustic soda in B, and the nitric oxide on coming in contact with the air in C is oxidized, and the nitric acid absorbed by the water In case the current of gas is too rapid, the escaping nitric acid is absorbed in D. After an hour the tubes *e* and *f* are disconnected, while the solutions in A and B are still boiling, and the nitric acid is titrated with dilute caustic soda (about ¼ normal). The vessel C must be well cooled during the whole experiment, which occupies about an hour and a half.

Good results were obtained with nitrates of potash and soda, both alone and mixed with ammonium sulphate, superphosphate, and amido compounds. With superphosphate the solution should be made slightly alkaline, to prevent the liberation of nitric acid.

Warington[1] has made a series of experiments on the original Schlösing process, for the purpose of testing its accuracy when small quantities of nitric acid have to be determined in the presence of organic substances, such for instance as in soils, the sap of beetroot, etc.; but instead of re-converting the nitric oxide into nitric acid as in the original method, he collected the gas either over caustic soda, as recommended by Reichardt, or over mercury, and ascertained its amount by measurement in Frankland's gas apparatus. The results obtained by Warington plainly showed that even in the most favourable circumstances the method as usually worked in Germany, either by the alkalimetric titration or by measurement of the gas, invariably gave results much too low, especially if the quantity of nitrate operated on was small, say 5 or 6 centigrams of nitre; moreover, when sugar or similar organic substance was present the resulting gas was very impure, and the distillates were highly coloured from the presence of some volatile products. The nitric oxide also suffered considerable diminution of volume when left for any length of time in contact with the distillate, especially when over caustic soda. This being the case, the following modification originally recommended by Schlösing was adopted in which CO_2 was employed, both to assist in expelling the air from the apparatus, and to chase out the nitric oxide produced.

The form of apparatus adopted by Warington is shown in fig. 46. The vessel in which the reaction takes place is a small tubulated receiver, the tubulure of which has been bent near its extremity to make a convenient junction with the delivery tube, which dips into a trough of mercury on the left. The long supply tube attached to the receiver is of small bore, and is easily filled by a ½ c.c. of liquid. The short tube to the right is also of small bore, and is connected by a rubber tube and clamp with an apparatus for the continuous production of carbon dioxide.

---

[1] *J. C. S.*, 1880, 468.

In using this apparatus the supply tube is first filled with strong HCl, and CO_2 is passed through the apparatus till a portion of the gas collected in a jar over mercury is found to be entirely absorbed by caustic potash. The current of gas is then stopped by closing the clamp to the right. A chloride of calcium bath at 140° is next brought under the receiver, which is immersed one-half or more in the hot fluid; the temperature of the bath is maintained throughout the operation by a gas burner placed beneath it. By allowing a few drops of HCl to enter the hot receiver, the CO_2 it contains is almost entirely expelled. A jar filled with mercury is then placed over the end of the delivery tube, and all is ready for the commencement of a determination.

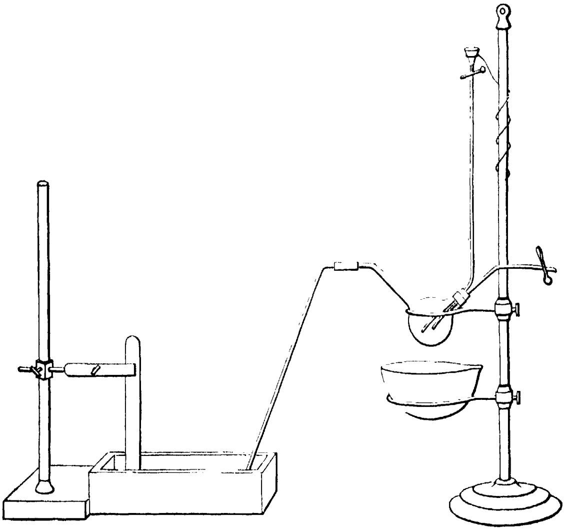

FIG. 46.

The nitrate, which should be in the form of a dry residue in a small beaker or basin, is dissolved in about 2 c.c.[1] of strong ferrous chloride solution, 1 c.c. of strong HCl is added, and the whole is then introduced into the receiver through the supply tube, being followed by successive rinsings with HCl, each rinsing not exceeding a ½ c.c., as the object is to introduce as small a bulk of liquid as possible. The contents of the receiver are in a few minutes boiled to dryness; a little CO_2

---

[1] Supposing the ferrous chloride to contain 2 gm. of iron per 10 c.c., then 1 c.c. of the solution will be nearly equivalent to 0·1207 gm. of nitre, or 0·0167 gm. of nitrogen. A considerable excess of iron should, however, always be used.

is admitted before dryness is reached, and again afterwards to drive over all remains of nitric oxide. If the gas is not to be analysed till next day, it is advisable to use more CO_2, so as to leave the nitric oxide diluted with several times its volume of that gas. As soon as one operation is concluded the apparatus is ready for another charge.

This mode of working presents the following advantages:—

(1) The volume of liquid introduced into the apparatus is much diminished, and with this of course the amount of dissolved air contributed from this source.

(2) By evaporation to dryness a complete reaction of the nitrate and ferrous chloride, and a perfect expulsion of the nitric oxide formed, is as far as possible attained.

(3) The nitric oxide in the collecting jar is left in contact with a much smaller volume of acid distillate, and its liability to absorption is greatly diminished by its dilution with CO_2.

The results obtained with this apparatus by Warington on small quantities of nitre alone, and when mixed with varying quantities of ammonium salts and organic substances including sugar, showed a marked improvement upon the method as usually carried out.

A further improvement has been made in this method by Warington,[1] and described by him as follows:—

The apparatus now employed is quite similar to that shown in fig. 46, with the only difference that the bulb retort in which the reaction takes place is now only 1⅜ inch in diameter, thus more exactly resembling the form employed by Schlösing. A bulb of this size is sufficient for the analysis of soil extracts; for determinations of nitrates in vegetable extracts a larger bulb is required.

The chief improvement consists in the use of CO_2 as free as possible from oxygen. The generator is formed of two vessels. The lower one consists of a bottle with a tubulure in the side near the bottom; this bottle is supported in an inverted position, and contains the marble from which the gas is generated. The upper vessel consists of a similar bottle standing upright; this contains the HCl required to act on the marble. The two vessels are connected by a glass tube passing from the side tubulure of the upper vessel to the inverted mouth of the lower vessel; the acid from the upper vessel thus enters below the marble. CO_2 is generated and removed at pleasure by opening a stop-cock attached to the side tubulure of the lower vessel, thus allowing HCl to descend and come in contact with the marble. The fragments of marble used have been previously boiled in water. The boiling is conducted in a strong flask. After boiling has proceeded some time, a rubber stopper is fixed in the neck of the flask, and the flame removed; boiling will then continue for some time in a partial vacuum. The lower reservoir is nearly filled with the boiled marble thus prepared. The HCl has been also well boiled, and before it is introduced into the upper reservoir it has dissolved in it a moderate quantity of cuprous chloride. As soon as the acid has been placed in the upper reservoir it is covered by a layer of oil.. The apparatus being thus charged is at once set in active work by opening the stop-cock of the marble reservoir; the acid descends, enters the marble reservoir, and the CO_2 produced drives out the air which is necessarily present at starting. As the acid reservoir is kept on a higher level than the marble reservoir, the latter is always under internal pressure, and leakage of air from without cannot occur.

The presence of the cuprous chloride in the hydrochloric acid not only ensures the removal of dissolved oxygen, but affords an indication to the eye of the maintenance of this condition. So long as the acid remains of an olive tint oxygen will be absent; but should the acid become of a clear blue-green, it is no longer certainly free from oxygen, and more cuprous chloride must be added.

---

[1] *J. C. S.*, 1882, 345.

A further slight improvement adopted consists in the use of freshly-boiled reagents, which are employed in as small a quantity as possible. When boiling the hydrochloric acid it is well to add a few drops of ferrous chloride, in order more certainly to remove any dissolved oxygen.

The mode of operation is as follows: The apparatus is fitted together, the long funnel tube attached to the bulb retort being filled with water. Connection is made with the glass stop-cock of the CO_2 generator by means of a short stout rubber tube, provided with a pinch-cock. The pinch-cock being opened, the stop-cock is turned till a moderate stream of bubbles rises in the mercury trough; the stop-cock is left in this position, and the admission of gas is afterwards controlled by the pinch-cock, pressure on which allows a few bubbles to pass at a time. The heated chloride of calcium bath is next raised, so that the bulb retort is almost submerged; the temperature, shown by a thermometer which forms part of the apparatus, should be 130° to 140°. By boiling small quantities of water or hydrochloric acid in the bulb retort in a stream of CO_2 the air present is expelled, the supply of gas must be stopped before the boiling has ceased, so as to leave little in the retort. Previous to very delicate experiments it is advisable to introduce through the funnel tube a small quantity of nitre, ferrous chloride, and hydrochloric acid, rinsing the tube with the latter reagent; any trace of oxygen remaining in the apparatus is then consumed by the nitric oxide formed, and after boiling to dryness, and driving out the nitric oxide with CO_2, the apparatus is in a perfect condition for a quantitative experiment.

Soil extracts may be used without other preparation than concentration. Vegetable juices, which coagulate when heated, require to be boiled and filtered, or else evaporated to a thin syrup, treated with alcohol and filtered. A clear solution being thus obtained, it is concentrated over a water bath to the smallest volume in a beaker of smallest size. As soon as cool, it is mixed with 1 c.c. of a cold saturated solution of ferrous chloride and 1 c.c. HCl, both reagents having been boiled and cooled immediately before use. In mixing with the reagents care must be taken that bubbles of air are not entangled; this is especially apt to occur with viscid extracts. The quantity of ferrous chloride mentioned is amply sufficient for most soil extracts, but it is well perhaps to use 2 c.c. in the first experiment of a series; the presence of a considerable excess of ferrous chloride in the retort is thus ensured. With bulky vegetable extracts more ferrous chloride should be employed; to the syrup from 20 gm. of mangel sap should be added 5 c.c. of ferrous chloride, and 2 c.c. of hydrochloric acid.

The mixture of the extract with ferrous chloride and HCl is introduced through the funnel tube and rinsed in with three or four successive ½ c.c. of HCl. The contents of the retort are then boiled to dryness, a little CO_2 being from time to time admitted, and a more considerable quantity used at the end to expel any remaining nitric oxide. The most convenient temperature is 140°, but in the case of vegetable extracts it is well to commence at 130°, as there is some risk of the contents of the retort frothing over. The gas is collected in a small jar over mercury. As soon as one operation is completed, the jar is replaced by another full of mercury, and the apparatus is ready to receive a fresh extract. A series of five determinations, with all the accompanying gas analyses, may be readily performed in one day. The bulb retort becomes encrusted with charcoal, when extracts rich in organic matter are the subject of analysis; it is best cleaned first with water, and then by heating oil of vitriol in it.

Mercury, contrary to the statement in most text-books, is gradually attacked by hydrochloric acid in the presence of air; the mercury in the trough is thus apt to become covered with a grey chloride, and it is quite necessary to keep the store of mercury in contact with sulphuric acid to preserve its mobile condition.

The gas analysis is of a simple character; the gas is measured after absorption of the CO_2 by potash, and again after absorption of the nitric oxide, the difference giving the amount of this gas. For the absorption of nitric oxide, a saturated solution of ferrous chloride was for some time employed. This method is not, however, perfectly satisfactory when the highest accuracy is required, the nitric oxide being generally rather under-estimated, unless the process of absorption is repeated with a fresh portion of ferrous chloride. The error is greater in proportion to the quantity of unabsorbed gas present. Thus, with a mixture of nitrogen and nitric oxide containing little of the former absorption of the nitric oxide by successive treatment with oxygen and pyrogallol over potash showed 97·8 per cent. of nitric oxide; while the same gas, analysed by a single absorption with ferrous chloride (after potash), showed 97·5 per cent. of nitric oxide. With a mixture containing more nitrogen, the oxygen method showed 65·9 per cent. of nitric oxide; while one absorption with ferrous chloride gave 61·2 per cent., and a second absorption, in which the ferrous chloride was plainly discoloured, 66·2 per cent. The use of ferrous chloride as an absorbent for nitric oxide has now been given up, and the oxygen method substituted. All the measurements of the gas are now made without shifting the laboratory vessel; the conditions are thus favourable to extreme accuracy.

The chief source of error attending the oxygen process lies in the small quantity of carbonic oxide produced during the absorption with pyrogallol; this error becomes negligible if the oxygen is only used in small excess. The difficulty of using the oxygen in nicely regulated quantity may be removed by the use of Bischof's gas delivery-tube. This may be made of a test-tube, having a small perforation half an inch from the mouth. The tube is partly filled with oxygen over mercury, and its mouth is then closed by a finely-perforated stopper, made from a piece of wide tube, and fitted tightly into the test-tube by means of a covering of rubber. When this tube is inclined, the side perforation being downwards, the oxygen is discharged in small bubbles from the perforated stopper while mercury enters through the side opening. Using this tube, the supply of oxygen is perfectly under control, and can be stopped as soon as a fresh bubble ceases to produce a red tinge in the laboratory vessel. The trials made with this apparatus have been very satisfactory.

If **nitrites** are to be determined by this method, it is necessary first to convert them into nitrates with excess of hydrogen peroxide, which is entirely destroyed by the subsequent evaporation to dryness.

4. By the Kjeldahl Process.

By the Gunning-Jodlbauer modified method described on p. 91 it is now quite possible to determine the nitrogen in commercial nitrates with great accuracy and very little personal attention.

5. Ulsch's Method.

This is a simple and ready plan of determining alkali nitrates, or the amount of them existing in manures when there is no salt of ammonia or other form of nitrogen present. It depends on the fact that when nitrate of soda or potash is boiled with dilute sulphuric acid, together with iron reduced by hydrogen, the nitrogen becomes converted into ammonium sulphate. The ammonia is then distilled off by boiling with caustic soda as in Kjeldahl's method.

Method of Procedure: 0·5 gm. of an alkali nitrate, dissolved in 25 c.c. of water, or a volume of manure solution containing about that quantity, which should not measure more than 25 or 30 c.c., is put into a small (150 c.c.) flask. 5 gm. of reduced iron and 20 c.c. of dilute sulphuric acid (1 : 3) are then added, and the flask placed in an inclined position and the reaction allowed to continue in the cold until effervescence ceases. The mixture is then boiled for 6 or 7 minutes, and allowed to cool. The liquid is then transferred to a Kjeldahl distilling flask, an excess of caustic soda with a few pieces of zinc added, and the ammonia collected in standard acid and titrated as usual in the Kjeldahl process. The calculation into nitrogen or alkali nitrate presents no difficulty.

Some operators have obtained high results by this method, owing to the reduced iron containing some form of nitrogen or ammonia. A *blank* experiment should therefore be made with the iron used to find whether such impurity exists. Brandt found that cyanogen was the offending agent, and this was removed by ignition of the iron again in hydrogen.

A 20 per cent. solution of *titanous chloride or sulphate* may be used as the reducing agent. The solution of nitrate is boiled with this reagent and excess of caustic soda in an ammonia distillation apparatus, the ammonia formed being received in standard acid as usual. A blank distillation should be made.

The official method[1] to be used in the analysis of fertilizers under the Fertilizers and Feeding Stuffs Act, 1906, is as follows :—

Nitrogen in Nitrates in the Absence of Ammonium Salts and of Organic Nitrogen.

1 gm. of the sample shall be placed in a half-litre Erlenmeyer flask with 50 c.c. of water, 10 gm. of reduced iron and 20 c.c. of sulphuric acid of 1·35 sp. gr.[2] shall be added. The flask shall be closed with a rubber stopper provided with a thistle tube, the head of which shall be half filled with glass beads. The liquid shall be boiled for five minutes, and the flask shall then be removed from the flame, any liquid that may have accumulated among the beads being rinsed back with water into the flask. The solution shall be boiled for three minutes more, and the beads again washed with a little water. The quantity of ammonia shall then be determined by distillation into standard acid after liberation with alkali. (Caustic Soda is generally used.)

---

[1] The Fertilizers and Feeding Stuffs (Methods of Analysis) Regulations, 1908. No. 964.

[2] Made by mixing 1 vol of 1·84 acid with 2 vols. of water.

6. Technical Method for the Schlösing Process with Alkali Nitrates and Nitrated Manures.

Wagner has arranged a simple form of the Schlösing method, which gives fairly good results and permits of rapid working.

The following is the slightly modified arrangement, as adopted at the Halle Agricultural Experiment Station, for the determination of nitrogen as nitrates in fertilizers.

A 250 c.c. flask is fitted with a two-hole rubber stopper. One hole carries an ordinary gas delivery-tube, and the other a thistle funnel, having a stop-cock below the funnel. The end of this tube is narrowed, and does not quite reach the liquid in the flask.

A solution of 200 gm. of iron wire in hydrochloric acid is made and diluted to 1 litre. 50 c.c. of this solution, and the same quantity of 10 per cent. HCl, are placed in the flask, and the air expelled by boiling. 10 c.c. of a standard solution of pure sodium nitrate, containing 25 gm. per litre, are then placed in the funnel, and allowed gradually to drop into the boiling solution of iron. A gas tube graduated to 100 c.c. is filled with 40 per cent. solution of caustic potash, and the nitric oxide collected in the usual way. When the nitre solution is nearly all dropped in, the funnel is filled with 10 per cent HCl, and run down drop by drop, and when no more nitric oxide is evolved the tube containing the gas set aside in a large jar containing distilled water. 10 c.c. of the solution to be tested are now put into the funnel, taking care that not more than 100 c.c. of gas will result. The gas is collected as before in a fresh tube precisely as in the case of the pure nitrate. In this manner ten or twelve determinations can be made with one and the same ferrous solution. Finally, a fresh test is made with standard nitre solution; the readings of the tubes are taken, and as they will all be of the same temperature and pressure no correction is necessary, all being allowed to cool to the same point. The comparison between the pure nitrate and the sample will afford the calculation.

7. Devarda's Method.[1]

The nitrate is reduced to ammonia by the evolution of hydrogen generated from alkali hydroxide and an alloy of aluminium with copper and zinc (Al 45, Cu 50, Zn 5), the ammonia being distilled into standard acid as in Kjeldahl's method. The alloy, which can be readily purchased, is brittle. It should be powdered sufficiently finely to pass through a No. 60 sieve, and five times the weight of the nitrate taken for the determination should be used. Cahen[2] distils the ammonia with steam, in preference to distillation by boiling.

METHOD OF PROCEDURE: About 0·5 gm. of the nitrate is dissolved in 110 c.c. of water in a Jena glass bulb flask, and 2-3 gm. of the alloy, 5 c.c. of alcohol, and 50 c.c. of caustic alkali (sp. gr. 1·3) added. The flask is then quickly connected to the Kjeldahl distilling apparatus and allowed to stand for 30 minutes, when the brisk reaction will be complete. The contents of the flask are then slowly raised to the boiling temperature, and steam passed for 30 minutes, when all the ammonia will have distilled over.

---

[1] *Z. a. C.*, 1894, **33**, 113.

[2] *Analyst*, 1910, **35**, 307.

8. Gasometric Determination, as Nitric Oxide, of Nitrogen in Nitrates and Nitrites.

1 c.c. NO at N.T.P. = 0·6254 mgm. N
" = 1·3402 " NO
" = 1·6975 " N_2O_3
" = 2·4121 " N_2O_5
" = 4·5140 " KNO_3
" = 3·7950 " $NaNO_3$
" = 2·8130 " HNO_3

The two following methods give the nitrogen existing as both nitrate and nitrite in the substances analysed.

(i) The Crum method. This method was described by W. Crum as far back as 1847. Originally devised for the analysis of nitrates and of gun-cotton, it was, in an improved form, used by Frankland and Armstrong for the determination of nitrates in water, for which purpose it is still largely used (see Water Analysis section).

(ii) Lunge's nitrometer method. This is fully described in the section on Technical Gas Analysis. It is used for the analysis of nitrous vitriol in sulphuric acid manufacture and for several other purposes.

NITRITES.

1. Iodimetric Method.

Dunstan and Dymond[1] have devised a method for the determination of N_2O_3 in organic and inorganic combination which is both simple in operation and accurate in results. The authors point out that although the inorganic nitrites may be accurately analysed by gasometric methods, or by permanganate, it is impossible to use such methods for the organic compounds or their alcoholic solutions. The reaction upon which the method depends is not new, being based on the following equation—

$$2HI + 2HNO_2 = 2H_2O + 2NO + I_2.$$

The liberated iodine is titrated with $^N/_{10}$ thiosulphate in the usual way. The chief merit in the process is the simple form of apparatus used, which is shown in fig. 47.

A stout glass flask, having a capacity of about 100 c.c., is closed by a tightly fitting rubber stopper, through which passes a piece of rather wide glass tubing (C), one end of which (that within the flask) is cut off obliquely, so that liquid may flow freely through it. The other end of the tube is connected by means of a piece of thick rubber tubing with a large glass tube, which forms a lipped funnel (A). A steel screw clamp (B) regulates communication between the funnel and the tube, and the short interval of rubber which is not occupied by glass tubing forms a hinge upon which the flask may be moved into a position at right-angles to the funnel, in order to mix by agitation the liquids which are introtroduced into the apparatus. The absence of any leak in the apparatus is ascertained by boiling about 50 c.c. of water in the flask until steam has continuously issued from the funnel for some few minutes, when the screw clip is quickly closed and simultaneously the source of heat is removed. A little water is now placed in the funnel and the flask is cooled by immersion in water. On sharply inverting the flask the "click" of the water against the airless flask should be quite distinct. No water should be drawn from the funnel or from any of the joints into the flask, and no diminution in the intensity of the "click" should be observed after the apparatus has been standing, neither when the flask is inverted and the funnel empty should any bubbles of air pass through into the liquid. Having thus proved the absence of any leak in the apparatus, it is ready for use. The flask is now free from all but mere traces of oxygen. A conclusive proof of this is obtained by boiling in the flask a solution of potassium iodide, acidified with diluted sulphuric acid, and then, after the closed flask has been cooled, the funnelremoved and its place taken by a smaller glass tube filled with air-free water, the apparatus is connected with a reservoir of pure nitric oxide. When the clamp is unscrewed nitric oxide is drawn into the flask, and should any oxygen be present nitrous acid will be produced, and consequently iodine will be set free. This experiment has often been made by the authors, who have failed to observe any but an insignificant trace of liberated iodine.

---

[1] *Pharm. Journ.* [3] 19, 741.

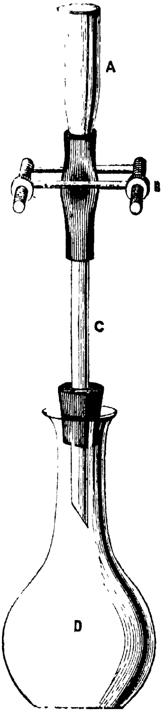

Fig. 47.

Method of Procedure: 5 c.c. of a 10 per cent. solution of potassiumiodide, 5 c.c. of a 10 per cent. solution of sulphuric acid, and 40 c.c. of water are introduced into the flask, which is securely fitted with the cork carrying the funnel and tube. The screw clip being open, and a free passage left for the escape of steam, the liquid is boiled. After a few minutes, when any iodine which may have been liberated has been expelled, and the upper part of the flask is completely filled with steam, which is also freely issuing from the funnel, the clip is tightly closed, and at the same moment the source of heat is removed. A little water is now put into the funnel, and also on the rim of the flask, as a safeguard against a possible minute leakage, and the vessel is cooled, by immersion in water. A solution containing a known weight of the nitrite (equivalent to about 0·1 gm. of nitrous acid) is placed in the funnel, and slowly drawn into the flask by cautiously unscrewing the clip. The liquid which adheres to the funnel is washed into the flask with recently boiled and air-free water, care being taken that during this operation no air is admitted into the flask. When experiments are being made with organic nitrites which are insoluble in water, they are dissolved in alcohol, and alcohol is also used to wash the funnel. When the nitrite is very volatile, a little cold alcohol should be put in the funnel, and the point of the pipette containing the nitrite should be held at the bottom of the funnel beneath the alcohol, and the liquid quickly drawn from the pipette into the flask. The nitrite having been introduced, the flask is well shaken and the liberated iodine is titrated with a standard solution of thiosulphate, small quantities of which are delivered from a burette into the funnel and gradually drawn into the flask; the screw clip renders it quite easy to admit minute quantities of the solution. As soon as the iodine is decolorized any standard solution remaining in the funnel is returned to the burette. Or the funnel may, before the titration is commenced, be replaced by the burette itself, and the standard solution delivered direct into the flask. Starch may be used as an indicator, but it is usually quite easy to observe the complete disappearance of the yellow colour of the dissolved iodine. From the volume of the standard solution used, the amount of nitrous acid is calculated from the equation before given.

It is obvious that the apparatus might be improved in several respects, as for example, by constructing it entirely of glass, with a ground stopper and tap, as well as by the use of a graduated funnel to deliver the standard solution, and also in other ways.

The authors quote numerous experiments, comparing the method with careful determinations of sodium and ethyl nitrites gasometrically, showing excellent results.

As a further test of the accuracy of the process, experiments were made with various organic nitrites of known purity. In each instance a solution of the nitrite was made by weight, and a weighed quantity was used for the determination. To prevent any loss of these volatile nitrites the experiments were conducted in the following manner: A well-stoppered bottle half filled with the alcohol corresponding to the nitrite [1] to be determined was weighed. Enough of the nitrite was now introduced by means of a pipette to constitute approximately a 2 per cent. solution, and the liquid again weighed. The exact strength of the solution having been thus determined, the contents of the bottle were well mixed, and the neck and stopper of the bottle dried. The bottle was now re-weighed, and about 2 c.c. of the solution removed by a pipette, care being taken not to wet the neck of the bottle. The liquid having been introduced into the flask without exposure to air, in the manner which has been previously described, the bottle containing the solution was again weighed. The results obtained with ethyl nitrite were:—

Taken.	Found.
0·088 gm.	0·089 gm.
0·176 ,,	0·179 ,,
0·113 ,,	0·115 ,,

---

[1] The corresponding alcohol was employed to prevent loss consequent on the occurrence of a reverse chemical change, which takes place when a lower homologous alcohol is mixed with the nitrite corresponding to a higher homologous alcohol; for example, a solution of amyl nitrite in ethyl alcohol soon becomes a solution of ethyl nitrite in amyl alcohol, from which the ethyl nitrite rapidly volatilizes.

2. Oxidation by Permanganate (Laird and Simpson).[1]

The method consists in oxidation of the nitrite in acid solution with excess of permanganate, reduction of the excess permanganate with excess of ferrous sulphate, oxalate. or hydrogen peroxide, and titration of the excess of reducing agent with permanganate.

An excess of $^{N}/_{10}$ permanganate solution is acidified with 10 or 20 c.c. of dilute sulphuric acid in a flask. The nitrite solution is then run in slowly with constant shaking. Excess of $^{N}/_{10}$ ferrous sulphate, hydrogen peroxide, or sodium oxalate solution is added, and the clear solution is finally titrated with permanganate. Ferrous sulphate is generally to be preferred, oxalate requiring titration at high temperature, and peroxide solutions being unstable. Hydrogen peroxide, however, can be used in nitric acid solutions, which allows of nitrite being determined in presence of barium. Chlorides do not interfere unless the concentration of chloride exceeds $/_2$.

3. Gasometric Method.

P. Frankland[2] adopts this method for the determination of nitrous acid in small quantity, but too large for colorimetric determination, and where also ammonia, organic matters, and nitrates may co-exist. It is based on the fact that when nitrous acid, together with excess of urea, is mixed with sulphuric acid in the cold, the reaction is

$$CO(NH_2)_2 + 2HNO_2 = 2N_2 + CO_2 + 3H_2O.$$

The decomposition is made in the Crum-Frankland shaking tube, described and figured in Part VII., and the evolved nitrogen gas measured in the usual gas apparatus. The ordinary nitrometer may also be used for large quantities of NO by the same method.

In the case of an ordinary alkali nitrite, the dry substance, or its solution evaporated to dryness, is mixed with excess of crystallized urea, and dissolved in about 2 c.c. of boiling water in a beaker, then transferred, with the rinsings, to the cup of the apparatus, and passed into the tube. A few c.c. of dilute sulphuric acid (1 : 5) are then passed in. A vigorous evolution of gas takes place, and continues for some 5 minutes; the gas is a mixture of nitrogen and carbonic anhydride. The decomposition is complete in 15 minutes. A solution of pure sodium hydrate (1 : 3) is now added through the cup, and the mixture violently shaken, until the CO_2 is absorbed. The gas and liquid are then transferred, by means of another mercury trough, to the laboratory vessel, and the gas, which is double the volume of the N existing as N_2O_3, measured in a gas apparatus, and its weight calculated in the usual way.

EXAMPLE: A solution of sodium nitrite was made and standardized with permanganate, the result being that 10 c.c. = 0·01346 gm. N. 10 c.c of the same solution were evaporated to dryness in a small beaker, about 0·2 gm. of urea added, the whole dissolved in 2 c.c. of hot water, which, with the rinsings, were transferred through the cup into the tube, treated with sulphuric acid and caustic soda, then transferred to the gas apparatus with the following results: Volume of N, 13·8 c.c.; mercurial pressure, 127·5 mm.; temperature, 17·7° C. The weight of N thus found, after the necessary corrections, was 0·01346 gm.

---

[1] *J. A. C. S.*, 1919, **41**, 524.

[2] *J. C. S.*, 1888, **53**, 364.

The Crum-Frankland mercury method, described in the section on Water Analysis, and in which the same shaking tube is used, does not distinguish between nitric and nitrous nitrogen; but P. Frankland required a method for the determination of nitrous acid in a mixture of nitrates, peptones, sugar, and various salts occurring in a solution used for cultivation of micro-organisms. The experiments carried out by him showed that when such a mixture was evaporated to dryness the loss of HNO_3 was considerable, and the results came out much too low. Further experiment, however, showed that the addition of a slight excess of caustic potash during evaporation prevented the loss of any HNO_2; and on the other hand the addition of a slight excess of ammonium chloride entirely destroyed it. Therefore by a combination of the mercury and the urea methods, the determination of nitric and nitrous acids may be satisfactorily accomplished, the destruction of the HNO_2 on the one hand being effected by excess of NH_4Cl, whilst on the other hand all loss of HNO_2 may be avoided by evaporation with caustic alkali. The mode of procedure has the advantage over all differential methods in that each acid is determined individually and independently of the other.

4. Colorimetric Methods.

The exceedingly delicate colorimetric methods of determining nitrites devised by Griess and others will be described in the section on Water Analysis.

DISSOLVED OXYGEN.

(See Water Analysis Section.)

HYDROGEN PEROXIDE, HYDROGEN DIOXIDE, OR HYDROXYL.

$H_2O_2 = 34·016.$

This substance is largely used in commerce and is commonly sold as of "10 volume" (3 per cent.) and "20 volume" strength, meaning thereby that the solution, when fully decomposed, yields ten times and twenty times its own volume respectively of oxygen. A still stronger preparation ("Perhydrol") can now be obtained which yields 100 times its own volume of oxygen: it contains 30 per cent. of H_2O_2.

Iodimetric Method.—Kingzett's[1] method of determining hydrogen peroxide is to add to its solution, strongly acidified with sulphuric acid, some potassium iodide, and to titrate the iodine set free with sodium thiosulphate and starch solution. The reaction is as follows:—

$$2HI + H_2O_2 = 2H_2O + I_2.$$

The function performed by the sulphuric acid is difficult of explanation, but the want of uniformity in the reaction experienced by many operators no doubt has arisen from the use of insufficient acid.

Method of Procedure: First dilute the peroxide solution, if necessary, to 2 volume strength (= 0·6 per cent. H_2O_2), then add 10 c.c.

---

[1] *J. C. S.*, 1880, 792.

of this gradually to 200 c.c. of dilute sulphuric acid (1 : 20) containing 2 gm. of potassium iodide. After standing 15 minutes titrate the liberated iodine with $^{N}/_{10}$ thiosulphate solution and starch.

In the case of a very weak solution it will be advisable to titrate with $^{N}/_{100}$ thiosulphate.

1 c.c. $^{N}/_{10}$ thiosulphate = 0·0017 gm. H_2O_2 or 0·0008 gm. O.

Permanganate Method.—The following reaction takes place when permanganate is added to a solution of hydrogen peroxide acidulated with sulphuric acid :—

$$5H_2O_2 + K_2Mn_2O_8 + 2H_2SO_4 = 5O_2 + 2MnSO_4 + K_2SO_4 + 8H_2O.$$

Thence (5 × 34·016) = 170·08 gm. H_2O_2 are equivalent to 316·06 gm. permanganate, or one litre of $^{N}/_{10}$ permanganate = 1·7008 gm. H_2O_2, and

1 c.c. $^{N}/_{10}$ permanganate = 0·0017 gm. H_2O_2.

As, however, hydrogen peroxide is usually supplied commercially as of "10 volume," etc., strength (see above), a factor can be found for calculating the "volume" strength from c.c. of permanganate required by 1 c.c. of peroxide, thus :—

100 c.c. of "10 volume" peroxide (specific gravity about 1·014) yield 1 litre of oxygen, which at N.T.P. weighs 1·4290 gm., and since 17 gm. of peroxide are equivalent to 8 gm. of oxygen, hydrogen peroxide by weight equivalent to 1·429 gm. of oxygen is

$$\frac{17}{8} \times 1{\cdot}429 = 3{\cdot}037 \text{ gm.}$$

Thence, 3·037 gm. of peroxide $= \frac{3{\cdot}037}{{\cdot}0017} = 1787$ c.c. $^{N}/_{10}$ permanganate.

Now, since $1787 \times \frac{4}{7} = 1021$, as against 1000 c.c. of oxygen yielded by 100 c.c. of "10 volume" peroxide, this factor may be used to get "volume" strength when an approximate result is all that is required. It should be noted that for the B.P. test the gas set free is to be measured at 60° F and normal pressure. 1000 c.c. of oxygen at N.T.P. become 1057 c.c. at 15·5° C. and normal pressure

EXAMPLE : 10 c.c. peroxide diluted to 100 c.c. and 10 c.c. of this (= 1 c.c. peroxide), pipetted into 30 c.c. dilute H_2SO_4 (1 : 5), then titrated with $^{N}/_{10}$ permanganate, of which 13·8 c.c. were required to give a permanent pink tinge.

$$13{\cdot}8 \times \frac{4}{7} = 7{\cdot}9,$$ which is the "volume" strength required.

Similarly, with the Kingzett Method, c.c. of $^{N}/_{10}$ thiosulphate required by 1 c.c. of peroxide multiplied by 0·56 gives "volume" strength.

Carpenter and Nicholson[1] report a series of experiments on the analysis of hydrogen peroxide, both by the iodine and permanganate methods.

The conclusion they arrive at is that the process of Kingzett is accurate, but in their hands somewhat tedious, owing to slow decomposition towards the end. Kingzett, however, states that if a volume of strong sulphuric acid equal to the peroxide taken be used, and especially if the dilute solution be slightly warmed, the reaction is complete in a few minutes, and this is my own experience.

---

[1] *Analyst*, 1884, **9**, 36.

A number of experiments have been made by C. Smith[1] as to the value of titrimetric and gasometric methods of ascertaining the amount of oxygen in H_2O_2, if it contains any preservative such as glycerin, boric acid, boroglycerin, salicylic acid, etc. The result was to show that the iodine and thiosulphate method gives accurate results with any of the preservatives tried, and in the presence of large proportions of glycerin, whereas the permanganate methods both titrimetric and gasometric were valueless.

The **free acid** in hydrogen peroxide solutions can be determined with sufficient accuracy for all practical purposes by direct titration in the cold with $^N/_{10}$ caustic alkali, using phenolphthalein as indicator.[2] The sole source of error is that due to dissolved carbon dioxide. An advantage of the method is that acetanilide (often present as a preservative) does not interfere, since it is not hydrolysed by cold caustic alkali.

Sodium Peroxide and Perborate.

$Na_2O_2 = 78$.

L. Archbutt[3] gives the results of some experiments on the determination of the available oxygen in sodium peroxide, and found that a near approximation to the truth could be obtained by simple titration with permanganate, the peroxide (one or two decigrams) being added to cold water acidified with H_2SO_4 contained in a porcelain dish, and $^N/_{10}$ permanganate dropped in with stirring until the colour became permanent; but a more exact method would be to add a known weight of the peroxide to an excess of $^N/_{10}$ permanganate, previously mixed with dilute H_2SO_4, and titrate for the excess of permanganate with $^N/_{10}$ oxalic acid. Archbutt, however, prefers to use the nitrometer, and recommends the following procedure: about 0·25 gm. of the substance is placed in the dry tube of the nitrometer flask, and in the flask itself about 5 c.c. of water, containing in suspension a few milligrams of precipitated cobalt sesquioxide; this latter reagent brings about a rapid and complete decomposition of the peroxide, the volume of oxygen evolved being the available oxygen in the sample.

For sodium perborate and perborate soap powders and the like H. Trickett[4] finds the iodimetric the most reliable method, but in the case of soap powders the soap must be previously removed. For direct application to perborates and soap powders, however, he suggests treating with hypochlorite solution in a nitrometer and measuring the volume of the liberated oxygen. Being in alkaline solution the presence of carbonates does not interfere. The results agree with those found by the iodimetric method. In the titration with permanganate, the best results are obtained by adding a slight excess of the perborate solution to a definite volume of permanganate solution acidified with sulphuric acid and titrating the excess with permanganate. The titration should be carried out at 15° to 20° C., and the acid concentration should be 5 per cent. of sulphuric acid on the total volume.

---

[1] *C. N.*, 1899, **80**, 194.

[2] Brown, *Analyst*, 1910, **35**, 497.

[3] *Analyst* 1895, **20**, 5.

[4] *Ibid.*, 1920, **45**, 88.

PHOSPHORIC ACID AND PHOSPHATES.

$P_2O_5 = 142{\cdot}08$.

THE determination of phosphoric acid volumetrically may be made with more or less accuracy by a variety of processes, among which may be mentioned that of Mohr as lead phosphate; the indirect method as silver phosphate (the excess of silver being found by thiocyanate); by standard uranium nitrate or acetate; by Pemberton's method as phospho-molybdate; or, when existing only as monocalcic phosphate, by standard alkali, as recommended by Mollenda or Emmerling. These processes are mainly useful in the case of fertilizers, or the raw phosphates from which manures are manufactured, and for P_2O_5 in urine, etc. For the purpose mentioned, that is to say, when in combination with alkali or alkaline earthy bases and moderate quantities of iron or alumina, phosphoric acid may be determined volumetrically with very fair accuracy, and with much greater rapidity than by gravimetric means as usually carried out.

1. Precipitation as Uranium Phosphate in Acetic Acid Solution.

This method is based on the fact that when uranium acetate or nitrate is added to a neutral solution of tribasic phosphoric acid, such, for instance, as sodium orthophosphate, the whole of the phosphoric acid is thrown down as yellow uranium phosphate Ur_2O_3, P_2O_5 + Aq. Should the solution, however, contain free mineral acid, it must be neutralized with an alkali, and an alkaline acetate added, together with excess of free acetic acid. In case of using ammonia and ammonium acetate, the whole of the phosphoric acid is thrown down as double phosphate of uranium and ammonia, having a light lemon colour, and the composition Ur_2O_3 $2(NH_4O)$, P_2O_5 + Aq. When this precipitate is washed with hot water, dried and ignited, the ammonia is entirely dissipated leaving uranium phosphate, which possesses the formula Ur_2O_3, P_2O_5, and contains in 100 parts 78·71 of uranium oxide and 21·29 of phosphoric acid. In the presence of fixed alkalis, instead of ammonia, the precipitate consists simply of uranium phosphate. By this method phosphoric acid may be completely removed from all the alkalis and alkaline earths; also, with a slight modification, from iron; not, however, satisfactorily from alumina when present in any quantity.

The details of the gravimetric process were fully described by me,[1] and immediately after the publication of that article, while employed in further investigation of the subject, I devised the volumetric method now to be described. Since that time it has come to my knowledge that Neubauer[2] and Pincus[3] had independently of each other and of myself arrived at the same process. This is not to be wondered at, if it be considered how easy the step is from the ordinary determination by weight to that by measure, when the delicate reaction between uranium and potassium ferrocyanide is known. Moreover, the great want of a really good volumetric process for phosphoric acid determination in place of those hitherto used has been felt by all who have had anything to do with the subject, and consequently the most would be made of any new method possessing so great a claim to accuracy as the gravimetric determination of phosphoric acid by uranium undoubtedly does.

---

[1] *C. N.*,1860, **1**, 97, 122. [2] *Archiv. fur wissenschaftliche Heilkunde*, **4**, 228.
[3] *Journal fur Prakt. Chem.*, **76**, 104.

Conditions under which approximate accuracy may be ensured.—Objections have been urged, not without reason, that this process is inaccurate, because varying amounts of saline substances have an influence upon the production of colour with the indicator. Again, that very different shades of colour occur with lapse of time. This is all true, and the method is unfortunately one of that class which requires uniform conditions; but when the source of irregularities is known, it is not difficult to obviate them. Therefore, it is absolutely essential that the standardizing of the uranium solution should be done under the same conditions as the analysis. For instance, a different volume of uranium solution will be required to give the colour in the presence of salts of ammonia from that which would be necessary with the salts of the fixed alkalis or alkaline earths. But if the standard solution is purposely adjusted with ammonia salts present in about the same proportion, the difficulties are less. Fortunately this can easily be done, and as the chief substances requiring analysis are more or less ammoniacal in their composition, such as urine, manures, etc, no practical difficulty need occur.

Excessive quantities of alkaline or earthy salts modify the colour, but especially is it so with acetate or citrate of ammonia. For this reason it is necessary to ensure the complete washing of the citromagnesium precipitate, where that method of separating P_2O_5 is adopted previous to titration. With all my experience of this method I cannot contend that it is an absolutely accurate one, but it is nevertheless a very rapid and convenient one for manure manufacturers in testing superphosphates and other phosphatic fertilizers.

2. Determination of Phosphoric Acid in combination with Alkali Bases, or in presence of small quantities of Alkaline Earths.

The necessary materials are—

(*a*) A standard solution of uranium 1 c.c. = 0·005 gm. P_2O_5.

(*b*) A standard solution of tribasic phosphoric acid.

(*c*) A solution of sodium acetate in dilute acetic acid, made by dissolving 100 gm. of sodium acetate in water, adding 50 c.c. of glacial acetic acid, and diluting to 1 litre. Exact quantities are not necessary.

(*d*) A freshly prepared solution of potassium ferrocyanide, or some finely powdered pure crystals of the same salt.

Standard Solution of Uranium.—This solution may consist either of uranium nitrate or acetate.[1] An approximate solution is obtained by using about 35 gm. of either salt to the litre. In using uranium nitrate it is imperative that the sodium acetate should be added in order to avoid the possible occurrence of free nitric acid in the solution. With acetate, however, it may be omitted at the discretion of the operator, but it is important that the method used in standardizing the uranium be invariably adhered to in the actual analysis. The solution should be perfectly clear and free from basic salt. Whether made from acetate or nitrate, it is advisable to include about 50 c.c. of pure glacial acetic, or a corresponding quantity of weaker acid, to each litre of solution; exposure to light has then less reducing action.

---

[1] Some operators object to the use of acetate, the reason for which I cannot understand. It stands to reason that, as with the use of nitrate there has to be a considerable quantity

My own practice is to use in all cases acetate solution, and dispense entirely with the addition of sodium acetate.

3. Titration of the Uranium Solution.

Standard Phosphoric Acid.—When the uranium solution is not required for phosphate of lime, it may be titrated upon ammonio-sodium phosphate (microcosmic salt) as follows: 5·88 gm. of the crystallized, non-effloresced salt (previously powdered and pressed between bibulous paper to remove any adhering moisture) are weighed, dissolved in water, and diluted to 1 litre. 50 c.c. of this solution will represent 0·1 gm. of P_2O_5.[1]

METHOD OF PROCEDURE: 50 c.c. of this solution are measured into a small beaker, 5 c.c. sodium acetate solution added if uranium nitrate is to be used, and the mixture heated to 90° or 100° C. The uranium solution is then delivered in from a burette, divided into $\frac{1}{10}$ c.c., until a test taken shall show the slight predominance of uranium. This is done by spreading a drop or two of the hot mixture upon a clean white level plate, and bringing in contact with the middle of the drop a thin glass rod moistened with the freshly made solution of ferrocyanide, or a dust of the powdered salt. The production of a faint brown tinge shows an excess of uranium, the slightest amount of which produces a brown precipitate of uranium ferrocyanide.

A second or third titration is then made in the same way, so as to arrive at the exact strength of the uranium solution, which is then diluted and re-titrated, until exactly 20 c.c. are required to produce the necessary reaction with 50 c.c. of phosphate.

Suppose 18·7 c.c. of the uranium solution have been required to produce the colour with 50 c.c. of phosphate solution, then every 18·7 c.c.

---

of sodium acetate used to prevent the formation of free HNO_3, the same conditions practically occur as if uranium acetate was used. The real reason, I believe is, that it is rather difficult to procure pure acetate. In the course of some thousands of titrations, I have found no advantage in using nitrate, and acetate needs no corrector to complicate the process as is the case with nitrate.

[1] W. B. Giles, who has had great experience in the determination of phosphoric acid in various forms, has called my attention to dihydric potassium phosphate, KH_2PO_4, as an excellent form of salt for a standard solution. The sample sent to me was in beautifully formed crystals which do not alter on exposure to the air, and makes a solution which keeps clear. Every one knows how unsatisfactory sodium phosphate is, both as to its state of hydration and its keeping qualities in solution; the microcosmic salt is better, but is open to objection on the score of indefinite hydration. If the potassium salt is used, a standard solution of the proper strength is made by dissolving 3·833 gm. in a litre.

will have to be diluted to 20 c.c. in order to be of the proper strength, or 935 to 1000. After dilution, two or three fresh trials must be made to ensure accuracy.

It is of considerable importance that the actual experiment for determining phosphoric acid by means of the uranium solution should be made with about the same bulk of fluid that has been used in standardizing the solution, and the same depth of colour aimed at in each case. Hence the proportions here recommended have been chosen, so that 50 c.c. of liquid shall contain 0·1 gm. of P_2O_5.

Standard Phosphoric Acid corresponding volume for volume with Standard Uranium.—This solution is obtained by dissolving 14·720 gm. of microcosmic salt in a litre, and is two and a half times the strength of the solution before described; it is used for residual titration in case the required volume of uranium is over-stepped in any given analysis.

A little practice enables the operator to tell very quickly the precise point; but it must be remembered that when the two drops are brought together for the production of the chocolate colour, however faint it seems at first, if left for some little time the colour increases considerably; but this has no effect upon the accuracy of the process, since the original standard of the solution has been based on an experiment conducted in precisely the same way.

METHOD OF PROCEDURE: In determining unknown quantities of P_2O_5 it is necessary to have an approximate knowledge of the amount in any given material, so as to fulfil as nearly as possible the conditions laid down above; that is to say, 50 c.c. of solution shall contain about 0·1 gm. P_2O_5, or whatever other proportion may have been used in standardizing the uranium.

The compound containing the P_2O_5 to be determined is dissolved in water; if no ammonia is present, 1 c.c. of 10 per cent. solution is dropped in and neutralized with the least possible quantity of acetic acid (also 5 c.c. of sodium acetate if uranium nitrate has to be used), and the volume made up to about 50 c.c., then heated to about 90° C. on the water-bath, and the uranium solution delivered in cautiously, with frequent testing as above described, until the faint brown tinge appears.

The first trial will give roughly the amount of solution required and taking that as a guide, the operator can vary the amount of liquid for the final titration, should the proportions be found widely differing from those under which the strength of the uranium was originally fixed.

Each c.c. of uranium solution = 0·005 gm. P_2O_5.

4. Determination of Phosphoric Acid in combination with Lime and Magnesia (Bones, Bone Ash, Soluble Phosphates, and other Phosphatic Materials free from Iron and Alumina).

The procedure in these cases differs from the foregoing in two respects only; that is to say, the uranium solution is preferably standardized by tribasic calcium phosphate; and in the process of titration it is necessary to add nearly the full amount of uranium required before heating the mixture, so as to prevent the precipitation of calcium phosphate, which is apt to occur in acetic acid solution when heated; or the modification adopted by Fresenius, Neubauer, and Luck, may be used, which consists in reversing the process by taking a measured volume of uranium, and delivering into it the solution of phosphate until a drop of the mixture ceases to give a brown colour with ferrocyanide. This plan gives, however, much more trouble, and possesses no advantage on the score of accuracy, because in any case at least two titrations must be performed, and the first being made somewhat roughly, in the ordinary way, shows within 1 or 2 c.c. the volume of standard uranium required; and in the final trial it is only necessary to add at once nearly the full quantity, then heat the mixture, and finish the titration by adding a drop or two of uranium at a time until the required colour is obtained.

This reversed process is strongly advocated by many operators, but except in rare instances I fail to see its superiority to the direct method for general use. The best modification to adopt in the reverse process is to use invariably an excess of uranium, and to titrate back with standard phosphate solution till the colour disappears; this avoids all the trouble of preparing and cleaning a burette for the solution to be analysed, and if a standard phosphate is made to correspond volume for volume with the uranium, an analysis may always be brought into order at any stage.

Standard Calcium Phosphate.—It is not safe to depend upon the usual preparations of tricalcium phosphate by weighing any given quantity direct, owing to uncertainty as to the state in which the phosphoric acid may exist; therefore, in order to titrate the uranium solution with calcium phosphate, it is only necessary to take rather more than 5 gm. of precipitated pure tricalcium phosphate such as is obtained in commerce, dissolve it in a slight excess of dilute hydrochloric acid, precipitate again with a slight excess of ammonia, re-dissolve in a moderate excess of acetic acid, then dilute to a litre; by this means is obtained a solution of acid monocalcium phosphate, existing under the same conditions as in the actual analysis. In order to ascertain the exact amount of tribasic phosphoric acid present in a given measure of this solution, two portions of 50 c.c. each are measured into two beakers, each holding about half a litre. A slight excess of solution of uranium acetate or nitrate is then added to each, together with about 10 c.c. of the acetic solution of sodium acetate; they are then heated to actual boiling on a hot-plate or sand-bath, the beakers filled up with boiling distilled water, and then set aside to settle, which occurs very speedily. The supernatant fluid should be faintly yellow from excess of uranium. When perfectly settled, the clear liquid is poured off as closely as possible without disturbing the precipitate, and the beakers again filled up with boiling water. The same should be done a third time, when the precipitates may be brought on two filters, and need very little further washing.

When the filtration is complete, the filters are dried and ignited apart from the precipitate, taking care to burn off all carbon. Before being weighed, however, the uranium-phosphate must be moistened with strong nitric acid, dried perfectly in the water-bath or oven, and again ignited; at first very gently, then strongly, so as to leave a residue of a pure light lemon colour when cold. This is uranium phosphate Ur_2O_3,

P_2O_5, the percentage composition of which is 78·71 of uranium oxide, and 21·29 of phosphoric acid.

The two precipitates are accurately weighed, and should agree to within a trifle. If they differ, the mean is taken to represent the amount of P_2O_5 in the given quantity of tricalcium phosphate, from which may be calculated the strength of the solution to be used as a standard. Of course any other accurate method of determining the P_2O_5 may be used in place of this.

The actual standard required is 5 gm. of pure tricalcium phosphate per litre; and it should be adjusted to this strength by dilution, after the actual strength has been found. In this way is obtained a standard which agrees exactly with the analysis of a superphosphate or other similar manure.

Standard Uranium Solution.—This is best adjusted to such strength that 25 c.c. are required to give the faint chocolate colour with ferrocyanide, when 50 c.c. of the standard acetic solution of calcium phosphate are taken for titration. Working in this manner each c.c. of uranium solution represents 1 per cent. of soluble tricalcium phosphate, when 1 gm. of a fertilizer is taken for analysis, because 50 c.c. of the calcium phosphate will contain monocalcium phosphate equal to 0·25 gm. of $Ca_3P_2O_8$ and will require 25 c.c. of uranium solution to balance it.

These standards are given as convenient for fertilizers, but they may be modified to suit any particular purpose.

THE METHOD WITH SUPERPHOSPHATES FREE FROM FE AND AL, EXCEPT IN MERE TRACES, is as follows: 10 gm. of the substance are weighed, placed in a small glass mortar and gently broken down by the pestle, cold water being used to bring it to a smooth cream. The material should not be ground or rubbed hard, which might cause the solution of some insoluble phosphate in the concentrated mixture. The creamy substance is washed gradually without loss into a measuring flask marked at 503·5 c.c., the 3·5 c.c. being the space occupied by the insoluble matters in an ordinary 25 to 30 per cent. superphosphate. The flask is filled to the mark with cold water, and shaken every few minutes during about half an hour. A portion is then filtered through a dry filter into a dry beaker, and 50 c.c. (= 1 gm. of fertilizer) measured into a beaker holding about 100 c.c. Sufficient 10 per cent. ammonia is then added to precipitate the monocalcium phosphate in the form of $Ca_3P_2O_8$ (in all ordinary superphosphates there is enough Ca present as sulphate to ensure this, and four or five drops of ammonia generally suffice to effect the precipitation). Acetic acid is then added in just sufficient quantity to render the liquid clear. Should traces of gelatinous $AlPO_4$ or $FePO_4$ appear at this stage, the liquid will be slightly opalescent; but this may be disregarded if only slight, as the subsequent heating will enable the uranium to decompose it. If more than traces are present, the method will not be accurate, and recourse must be had to separation by the citro-magnesium solution.

While the liquid is still cold, a measured volume of the standard uranium is run in with stirring, and drops are occasionally taken out with a glass rod, and brought in contact with some ferrocyanide indicator spotted on a white plate until a faint colour appears. The beaker is then placed in the water-bath for a few minutes, and the mixture again tested with the indicator; after heating in this way the testing ought to show no colour. More uranium is then added with stirring, and drop by drop till the proper reaction occurs. This titration is only a guide for a second, which may be made more accurate by running in at once very nearly the requisite volume of uranium.

This operation may be reversed, if so desired, by making the clear solution of phosphate up to a definite volume (say 60 c.c.), and running it from a burette into a measured volume of uranium until a test taken shows no colour.

5. Determination of Phosphoric Acid in Minerals or other materials containing Iron, Alumina, or other interfering substances.

In order to make use of any volumetric process for this purpose the phosphoric acid must be separated. As has been already described, this may be done either as molybdenum phosphate followed by solution in NH_3, and again precipitated with ordinary magnesia mixture, or direct separation by the citro-magnesium mixture described below. In either case the ammonio-magnesium salt is dissolved in the least possible quantity of nitric or hydrochloric acid, neutralized with ammonia, acidified with acetic acid, and the titration with uranium carried out as before described.

6. Pemberton's Molybdic Method.

This method[1] is one which requires great delicacy of manipulation, but gives excellent results with all the alkali or alkaline earthy phosphates.

The method is as follows:—[2]

The solutions required are:—

Molybdate Solution.—Dissolve 100 gm. of molybdic acid in 144 c.c. of ammonia, sp. gr. 0·90, and 271 c.c. of water; slowly, and with constant stirring, pour the solution thus obtained into 489 c.c. of nitric acid (sp. gr. 1·42), and 1148 c.c. of water. Keep the mixture in a warm place for several days, or until a portion heated to 40° C. deposits no yellow precipitate of ammonium phosphomolybdate. Decant the solution from any sediment and preserve in glass-stoppered vessels.

For use add to 100 c.c. of this solution 5 c.c. of nitric acid, sp. gr. 1·42. Filter each time before using.

Standard Potassium Hydroxide Solution.—This solution contains 18·171 gm. of potassium hydroxide to the litre. It is prepared by diluting 323·85 c.c. of normal potash (which has been freed from carbonates by barium hydroxide) to 1 litre. 100 c.c. of the solution should neutralize 32·38 c.c. of normal acid. One c.c. of this is equal to 0·001 gm. of P_2O_5, or 1 per cent. if 0·1 gm. of the substance is taken for analysis. Normal soda may be used instead of potash.

Standard Nitric Acid Solution.—This solution should correspond in strength to the standard alkali solution, or may be one half that strength. It is standardized by titrating against that solution, using phenolphthalein as indicator. Any mineral acid may be used.

---

[1] *J. A. C. S.*, 1894, 16, 278.

[2] *Bulletin* No. 107, U.S. Dept. Agric.

If a soluble phosphate is to be analysed, dissolve 1 gm. in water and make up to 250 c.c. 25 c.c. of this solution, representing 0·1 gm. of the substance, is taken for analysis. If the phosphate is in an insoluble compound or organic substance, 2 gm. are treated by one of the methods given below. After solution, cool, dilute to 200 or 250 c.c., mix and pour on a dry filter.

Total Phosphoric Acid.—(*a*) Dissolve in 30 c.c. of concentrated nitric acid and a small quantity of hydrochloric acid and boil until organic matter is destroyed.

(*b*) Evaporate with 5 c.c. of magnesium nitrate, ignite, and dissolve in hydrochloric acid.

(*c*) Add 30 c.c. of concentrated hydrochloric acid, heat, and add cautiously, in small quantities at a time, about 0·5 gm. of finely pulverized potassium chlorate to destroy organic matter.

(*d*) Dissolve in from 15 to 30 c.c. of strong hydrochloric acid and from 3 to 10 c.c. of nitric acid. This method is recommended for fertilizers containing much iron or aluminium phosphate.

DETERMINATION.—(1) For percentages of 5 or below use an aliquot volume corresponding to 0·4 gm. of substance; for percentages between 5 and 20 use a volume corresponding to 0·2 gm. of substance, and for percentages above 20 use a volume corresponding to 0·1 gm. of substance. Add from 5 to 10 c.c. of nitric acid, depending on the method of solution (or the equivalent in ammonium nitrate), nearly neutralize with ammonia, dilute to from 75 to 100 c.c., heat in water-bath to 60°-65° C., and for percentages below 5 add from 20 to 25 c.c. of freshly-filtered molybdate solution. For percentages between 5 and 20 add from 30 to 35 c.c. of molybdate solution; stir, let stand about 15 minutes, filter *at once*, wash once or twice with water by decantation, using from 25 to 30 c.c. each time, agitating the precipitate thoroughly and allowing to settle; transfer to filter and wash with cold water until two fillings of the filter do not greatly diminish the colour produced with phenolphthalein by one drop of the standard alkali. Transfer precipitate and filter to beaker or precipitating vessel, dissolve in small excess of standard alkali, add a few drops of phenolphthalein solution, and titrate with standard acid.

(2) Proceed as directed in (1), with this exception: Heat in a water-bath at 45° to 50° C., add the molybdate solution, and allow to remain in the bath with occasional stirring for 30 minutes.

(3) Proceed as in (1) to the point where the solution is ready to place in the water-bath. Then cool solution to room temperature, add molybdate solution at the rate of 75 c.c. for each 0·1 gm. of phosphoric acid present, place the stoppered flask containing the solution in a shaking apparatus and shake for 30 minutes at room temperature, filter at once, wash, and titrate as in preceding method.

Water-soluble Phosphoric Acid.—Place 2 gm. of the sample on a 9-cm. filter, wash with successive small portions of water, allowing each portion to pass through before adding more, until the filtrate measures about 250 c.c. If the filtrate be turbid, add a little nitric acid. Make up to any convenient definite volume, mix well, use an aliquot portion of the solution corresponding to 0·2 or 0·4 gm., add 10 c.c. of concentrated nitric acid and ammonia until a slight permanent precipitate is formed, dilute to 60 c.c., and proceed as under the preceding method (1).

Citrate-insoluble Phosphoric Acid.—Make the solution according to the directions given before and determine the phosphoric acid in an aliquot volume corresponding to 0·4 gm., as directed for total phosphates.

Determination in Acidulated Samples.—Heat 100 c.c. of strictly neutral ammonium citrate solution of 1·09 sp. gr. to 65° C. in a flask placed in a warm water-bath, keeping the flask loosely stoppered to prevent evaporation. When the citrate solution in the flask has reached 65° C. drop into it the filter containing the washed residue from the water-soluble phosphate determination, close tightly with a smooth rubber stopper, and shake violently until the filter paper is reduced to a pulp. Place the flask in the bath and maintain it at such a temperature that the contents of the flask will stand at exactly 65° C. Shake the flask every 5 minutes.

At the expiration of exactly 30 minutes from the time the filter and residue are introduced, remove the flask from the bath and immediately filter the contents as rapidly as possible; wash thoroughly with water at 65° C. Then proceed as under (*a*) or (*b*).

(*a*) Transfer the filter and its contents to a crucible, ignite until all organic matter is destroyed, add from 10 to 15 c.c. of strong hydrochloric acid, and digest until all phosphate is dissolved, or (*b*) return the filter with contents to digestion flask, add from 30 to 35 c.c. of strong nitric acid, and from 5 to 10 c.c. of strong hydrochloric acid, and boil until all phosphate is dissolved. Dilute to 200 c.c., mix well, and pass through a dry filter. Take a definite portion of the filtrate and proceed as under *total phosphoric acid.*

Determination in Non-acidulated Samples.—Treat 2 gm. of the phosphatic material without previous washing with water, precisely in the way above described, except that in case the substance contains much animal matter (bone, fish, etc.), the residue, insoluble in ammonium citrate, is to be dissolved by the treatment described under (*b*), or by digestion with concentrated sulphuric acid in the presence of a small quantity of sodium or potassium nitrate.

Citrate-soluble Phosphoric Acid.—The sum of the water-soluble and citrate-insoluble subtracted from the total phosphoric acid, gives the citrate-soluble phosphoric acid.

Richardson[1] states that when phosphoric acid is determined in acid phosphate by the Pemberton volumetric method or its usual modifications, the results do not agree with those obtained gravimetrically by the A. O. A. C. method, and the error frequently amounts to + 1 per cent. P_2O_5.

The disturbing substance is probably sulphuric acid, and if this be removed by barium chloride, the volumetric method may be applied and accurate results obtained.

Richardson recommends the following procedure:—

---

[1] *J. A. C. S.*, 1907, **29**, 1314, and Schimpf, "*Volumetric Analysis*," p. 320.

Weigh 2 gm. into a 250 c.c. flask, digest by boiling with 30 c.c. of concentrated nitric acid and 5 c.c. concentrated hydrochloric acid, then add 10 c.c. water and boil for 5 minutes. Add 25 to 30 c.c. of 10 per cent. barium chloride, cool, and make up to volume. Filter through a dry filter, rejecting the first portion of the filtrate, and take 25 c.c. for the determination. From this point on follow the Pemberton Method as above.

Determination of Phosphoric Acid in any Form in Food-stuffs.—Neumann's method, as modified by Plimmer and Bayliss,[1] is considered by Dr. Monier-Williams to be by far the most accurate and expeditious for this purpose. The method has been described by Dr. Monier-Williams[2] as follows:—

A weighed quantity of the substance, which should contain not more than 25 mgm. of phosphoric anhydride (P_2O_5), is treated in a round-bottomed Jena flask of about 1 litre capacity with 5 c.c. concentrated sulphuric acid and an excess of strong HNO_3 (1·40 sp. gr.). With some substances the action takes place at once with copious evolution of red fumes, and may be moderated by addition of water.

The contents of the flask are strongly heated over a free flame, with constant shaking and repeated additions of small quantities of nitric acid, until a clear liquid is obtained which does not darken on further heating. This operation lasts about 10 to 15 minutes. The liquid is then treated with 70 c.c. of water and 25 c.c. of 50 per cent. ammonium nitrate solution, warmed to about 80° C., and the phosphoric acid precipitated with 25 to 30 c.c. of 10 per cent. ammonium molybdate solution.

The mixture is thoroughly shaken and cooled, and the precipitate filtered off by suction through asbestos on a Gooch crucible. It is washed several times with cold distilled water until free from acid, and then transferred together with the asbestos to a conical flask, with a small quantity of distilled water. $^N/_2$ NaOH is added from a burette in quantity more than sufficient to dissolve the precipitate, the liquid is boiled until all the ammonia has been driven off, cooled, and titrated back with $^N/_2$ H_2SO_4 and phenolphthalein.

$$1 \text{ c.c. } ^N/_2 \text{ NaOH} = 0{\cdot}001268 \text{ gm. } P_2O_5.$$

He had used this method for a great many determinations of P_2O_5 in flour, and had found it to be quicker and more accurate than the gravimetric methods, while there could be no formation of meta- or pyrophosphate. It was, also, in his opinion, much better than the Carius method, and as far as he could see, could be used for the determination of P_2O_5 in any form, organic or inorganic.

7. Determination of Phosphoric Acid by Silver Nitrate (Holleman).[3]

J. M. Wilkie[4] has modified Holleman's method, in which phosphoric acid or an alkali-metal phosphate is converted to the di-alkali metal salt by means of caustic soda, the silver phosphate precipitated in presence of sodium acetate, and the residual silver determined in the filtrate by Volhard's method. This method usually gives high results, but the following mode of operating gives accurate results :—

---

[1] *J. of Physiology*, 1906, **33**, 439.

[2] *Analyst*, 1911, **36**, 582.

[3] *Z. a. C.*, 1895, **34**, 85, and *J. S. C. I.*, 1894, **13**, 763 and 843.

[4] *J. S. C. I.*, 1910, **29**, 794.

Phenolphthalein is added to the solution containing the phosphate, then strong caustic soda till the liquid is just pink, when the colour is discharged by dilute nitric acid, added drop by drop. In presence of calcium the precipitated phosphate is the best indicator, nitric acid being added until the precipitate is just dissolved. Excess of silver solution is next added, followed by 10 c.c. of approximately $^N/_{10}$ sodium acetate; then approximately $^N/_{10}$ caustic soda is run in, while shaking, till the liquid is faintly alkaline to phenophthalein. Two c.c. of $^N/_{10}$ sulphuric acid are added to this solution, which is diluted to 150 c.c., mixed, filtered, and the silver in the solution determined by Volhard's method. The method is not available in the presence of appreciable amounts of aluminium or iron. Chlorides must be allowed for, but may be got rid of by adding excess of sulphuric acid to the phosphate solution and evaporating at 100° C. The determination is made as above, after addition of nitric acid.

According to J. Rosin[1] the reaction proceeds thus :—

$$3Na_2HPO_4 + 6AgNO_3 = 2Ag_3PO_4 + 6NaNO_3 + H_3PO_4.$$

After addition of silver nitrate and shaking thoroughly, he neutralizes with zinc oxide.

8. Other Volumetric Methods for the Determination of Phosphoric Acid.

Several methods depending upon alkalimetry have been suggested, but beyond those quoted under Phosphoric Acid, p. 120, I have found none easy or reliable in practice.

A. Grete[2] titrates phosphoric acid in acid solution with alkaline molybdate solution in the presence of glue. It is claimed that this method has been thoroughly tested in practice since 1888, and that 20 determinations can be made in an hour, with results equal in accuracy to those obtained by the gravimetric process.

Two iodimetric methods described depend upon the interaction of standard sodium hypobromite solution in the presence of potassium iodide (1) with ammonium phospho-molybdate (P. Artmann)[3] and (2) with ammonium magnesium phosphate (R. Brandis).[4]

9. Iodimetric Determination of Phosphites and Hypophosphites (Boyer and Bauzil).[5]

The method is based on the fact that hypophosphorous acid is oxidized by iodine in acid solution to phosphorous acid and no further, but in the presence of an alkali (sodium bicarbonate) the oxidation proceeds to phosphoric acid.

---

[1] *J. A. C. S.*, 1911, **33**, 1099 (*Abstr. Analyst*, 1911, **36**, 472).

[2] *Ber.*, 1909, **42**, 3106, and *J. S. C. I.*, 1909, **28**, 1105.

[3] *Z. a. C.*, 1910, **49**, 1, and *J. S. C. I.*, 1910, **29**, 455.

[4] *Z. a. C.*, 1910, **49**, 152, and *J. S. C. I.*, 1910, **29**, 455.

[5] *J. Pharm. Chim.*, 1918, **18**, 321.

Hypophosphites.—10 c.c. of the solution containing 0·1 gm. of the hypophosphite are treated in a stoppered flask with 10 c.c. of 25 per cent. sulphuric acid and 30 c.c. of $^N/_{10}$ iodine solution, the mixture allowed to stand in the dark for 10 hours, and the excess of iodine then titrated with $^N/_{10}$ thiosulphate solution. 1 c.c. $^N/_{10}$ iodine = 0·0033 gm. $HP(OH)_2$.

Phosphites.—10 c.c. of the solution containing about 0·1 gm. of the salt are treated with 10 c.c. of 5 per cent. sodium bicarbonate solution and 20 c.c. of $^N/_{10}$ iodine solution. After two hours 10 c.c. of 10 per cent. acetic acid are added, and the excess iodine titrated. 1 c.c. $^N/_{10}$ iodine = 0·0041 gm. H_2PHO_3. The method may be applied to mixtures of the two salts.

SELENIUM.

Se = 79·2.

THE most accurate results in the determination of selenious acid are obtained when the substance is distilled with hydrochloric acid and an excess of potassium iodide (four times the quantity required by theory), and the liberated iodine then titrated both in the receiver and in the residue. The indirect iodimetric method of Gooch and Pierce, in which the selenious acid is heated with a known excess of potassium iodide in the presence of potassium hydrogen arsenate and sulphuric acid, and the arsenious acid formed then titrated with iodine solution after neutralization, also gives accurate results if carried out as a distillation process.

In the oxidation of selenious acid by permanganate in alkaline solution, there is always some loss of oxygen when the hot mixture is acidified previous to the titration of the excess of permanganate. The results, therefore, are inaccurate.

When selenious acid is titrated with titanium trichloride solution, hydrogen selenide is formed, and consequently this method is unsatisfactory.

The best method for the determination of *selenic acid* consists in reduction with hydriodic acid. 100 c.c. of the solution are treated with 10 c.c. of strong hydrochloric acid and an excess of potassium iodide (5 gm. for each 0·1 gm. selenium), the mixture distilled in a current of CO_2, and the iodine titrated in both the receiver and the residue.[1]

SILVER.

Ag = 107·88.

1 c.c. $^N/_{10}$ sodium chloride = 0·010788 gm. silver.
" " = 0·016989 gm. silver nitrate.

1. Precipitation with $^N/_{10}$ Sodium Chloride (Gay-Lussac).

THE determination of silver is precisely the converse of the operations described under Chlorine (p. 183), and the process may either be concluded by adding the sodium chloride till no further precipitate is produced, or potassium chromate may be used as an indicator. In the latter case, however, it is advisable to add the salt solution in excess, then a drop or two of chromate, and titrate residually with $^N/_{10}$ silver, till the red colour is produced, for the excess of sodium chloride.

---

[1] Moser and Prinz, *Z. a. C.*, 1918, 57, 277.

2. By Ammonium Thiocyanate.

The principle of this method is fully described on p. 150, *et seq.*, and need not further be alluded to here. The author of the method (Volhard) states that comparative tests made by this method and by that of Gay-Lussac gave equally exact results, both being controlled by cupellation, but claims for this process that the end of the reaction is more easily distinguished, and that there is no labour of shaking, or danger of decomposition by light, as in the case of chloride. My own experience fully confirms this. The method is now adopted largely in place of Gay-Lussac's for silver assays.

3. Determination of Silver, in Ores and Alloys, by Starch Iodide (Method of Pisani and F. Field).

If a solution of blue starch iodide be added to a neutral solution of silver nitrate, while any of the latter is in excess the blue colour disappears, the iodine entering into combination with the silver; as soon as all the silver is thus saturated, the blue colour remains permanent, and marks the end of the process. The reaction is very delicate, and the process is more especially applicable to the analysis of ores and alloys of silver containing lead and copper, but not mercury, tin, iron, manganese, antimony, arsenic, or gold in solution.

The solution of starch iodide, devised by Pisani, is made by rubbing together in a mortar 2 gm. of iodine with 15 gm. of starch and about 6 or 8 drops of water, putting the moist mixture into a stoppered flask, and digesting in a water-bath for about an hour, or until it has assumed a dark bluish-grey colour; water is then added till all is dissolved. The strength of the solution is then ascertained by titrating it with 10 c.c. of a solution of silver containing 1 gm. in the litre, to which a portion of pure precipitated calcium carbonate is added; the addition of this latter removes all excess of acid, and at the same time enables the operator to distinguish the end of the reaction more accurately. The starch iodide solution should be of such a strength that about 50 c.c. are required for 10 c.c. of the silver solution (= 0·01 gm. silver).

F. Field,[1] who discovered the principle of this method simultaneously with Pisani, used a solution of iodine in potassium iodide with starch. Those who desire to make use of this plan can use the $^N/_{10}$ and $^N/_{100}$ solutions of iodine described on p. 136.

In the analysis of silver containing copper, the solution must be considerably diluted in order to weaken the colour of the copper; a small measured portion is then taken, calcium carbonate added, and starch iodide till the colour is permanent. It is best to operate with from 60 to 100 c.c., containing not more than 0·02 gm. silver; when the quantity is much greater than this, it is preferable to precipitate the greater portion with $^N/_{10}$ sodium chloride, and to complete with starch iodide after filtering off the chloride. When lead is present with silver in the nitric acid solution, add sulphuric acid, and filter off the lead sulphate, then add calcium carbonate to neutralize excess of acid, filter again if necessary, then add fresh carbonate and titrate as described above.

---

[1] *C. N.*, 1860, 2, 17.

4. Assay of Commercial Silver (Plate, Bullion, Coin, etc.). Gay-Lussac's Method modified by J. G. Mulder.

For more than thirty years Gay-Lussac's method of determining silver in its alloys has been practised intact, at all the European mints, under the name of the "humid method," in place of the old system of cupellation. During that time it has been regarded as one of the most exact methods of quantitative analysis. The exhaustive researches of Mulder, however, have shown that it is capable of even greater accuracy than has hitherto been supposed.

The principle of the process is the same as described on p. 141, depending on the affinity which chlorine has for silver in preference to all other substances, and resulting in the formation of silver chloride, a compound insoluble in dilute acids, and which readily separates itself from the liquid in which it is suspended.

The plan originally devised by the illustrious inventor of the process for assaying silver, which is still followed, is to consider the weight of alloy taken for examination to consist of 1000 parts, and the question is to find how many of these parts are pure silver. This empirical system was arranged for the convenience of commerce, and being now thoroughly established, it is the best plan of procedure. If, therefore, a standard solution of salt be made of such strength that 100 c.c. will exactly precipitate 1 gm. of silver, it is manifest that each $\frac{1}{10}$ c.c. will precipitate 1 mgm. or $\frac{1}{1000}$ part of the gram taken; and consequently in the analysis of 1 gm. of any alloy containing silver, the number of $\frac{1}{10}$ c.c. required to precipitate all the silver out of it would be the number of thousandths of pure silver contained in the specimen.

In practice, however, it would not do to follow this plan precisely, inasmuch as neither the measurement of the standard solution nor the ending of the process would be gained in the most exact manner; consequently, a decimal solution of salt, one-tenth the strength of the standard solution, is prepared, so that 1000 c.c. will exactly precipitate 1 gm. of silver, and, therefore, 1 c.c. 1 mgm.

The silver alloy to be examined (the composition of which must be approximately known) is weighed so that about 1 gm. of pure silver is present: it is then dissolved in pure nitric acid by the aid of a gentle heat, and 100 c.c. of standard solution of salt added from a pipette in order to precipitate exactly 1 gm. of silver; the bottle containing the mixture is then well shaken until the silver chloride has curdled, leaving the liquid clear.

The question is now: Which is in excess, salt or silver? A drop of decimal salt solution is added, and if a precipitate be produced 1 c.c. is delivered in, and after clearing, another, and so on as long as a precipitate is produced. If on the other hand, the one drop of salt produced no precipitate, showing that the pure silver present was less than 1 gm., a decimal solution of silver is used, prepared by dissolving 1 gm. pure silver in pure nitric acid and diluting to 1 litre. This solution is added after the same manner as the salt solution just described, until no further precipitate appears; in either case the quantity of decimal solution used is noted, and the results calculated in thousandths for 1 gm. of the alloy.

The process thus shortly described is that originally devised by Gay-Lussac, and it was taken for granted that, when equivalent chemical proportions of silver and sodium chloride were brought thus in contact, every trace of the metal was precipitated from the solution, leaving sodium nitrate and free nitric acid only in solution. The researches of Mulder, however, go to prove that this is not strictly the case, but that when the most exact chemical proportions of silver and salt are made to react on each other, and the chloride has subsided, a few more drops of either salt or silver solution will produce a further precipitate, indicating the presence of both silver nitrate and sodium chloride in a state of equilibrium, which is upset on the addition of either salt or silver. Mulder decides, and no doubt rightly, that this peculiarity is owing to the presence of sodium nitrate, and varies somewhat with the temperature and state of dilution of the liquid.

It therefore follows that when a silver solution is carefully precipitated, first by concentrated and then by dilute salt solution, until no further precipitate appears, the clear liquid will at this point give a precipitate with dilute silver solution, and if it be added till no further cloudiness is produced, it will again be precipitable by dilute salt solution.

Example: Suppose that in a given silver analysis the decimal salt solution has been added so long as a precipitate is produced, and that 1 c.c. (= 20 drops of Mulder's dropping apparatus) of decimal silver is in turn required to precipitate the apparent excess, it would be found that when this had been done, 1 c.c. more of salt solution would be wanted to reach the point at which no further cloudiness is produced by it, and so the changes might be rung time after time, if, however, instead of the last 1 c.c. (= 20 drops) of salt, half the quantity be added, that is, to say 10 drops (= ½ c.c.), Mulder's so called neutral point is reached; namely, that in which, if the liquid be divided in half, both salt and silver will produce the same amount of precipitate. At this stage the solution contains silver chloride dissolved in sodium nitrate, and the addition of either salt or silver expels it from solution.

A silver analysis may therefore be concluded in three ways—

(1) By adding decimal salt solution until it just ceases to produce a cloudiness.

(2) By adding a slight excess of salt, and then decimal silver till no more precipitate appears.

(3) By finding the neutral point.

According to Mulder the latter is the only correct method, and preserves its accuracy at all temperatures up to 56° C. (= 133° Fahr.), while the difference between 1 and 3 amounts to ½ a mgm., and that between 1 and 2 to 1 mgm. on 1 gm. of silver at 16° C. (= 60·8° Fahr.), and is seriously increased by variation of temperature.

It will readily be seen that much more trouble and care is required by **Mulder's** method than by that of **Gay-Lussac**, but as a compensation, much greater accuracy is obtained.

On the whole it appears to me preferable to weigh the alloy so that slightly more than 1 gm. of silver is present, and to choose the ending No. 1, adding drop by drop the decimal salt solution until just a trace of the precipitate is seen, and which, after some practice, is known by the operator to be final. It will be found that the quantity of salt solution used will slightly exceed that required by chemical computation; say 100·1 c.c. are found equal to 1 gm. of silver, the operator has only to calculate that quantity of the salt solution in question for every 1 gm. of silver he assays in the form of alloy, and the error produced by the solubility of silver chloride in sodium nitrate is removed.

If the decimal solution has been cautiously added, and the temperature not higher than 17° C. (62° Fahr.), this method of conclusion is as reliable as No. 3, and free from the possible errors of experiment; for it requires a great expenditure of time and patience to reverse an assay two or three times, each time cautiously adding the solutions drop by drop, then shaking and waiting for the liquid to clear, besides the risk of discolouring the silver chloride, which would at once vitiate the results.

The decimal silver solution, according to this arrangement, would seldom be required; if the salt has been incautiously added, or the quantity of alloy too little to contain 1 gm. pure silver, then it is best to add once for all 2, 3, or 5 c.c., according to circumstances, and finish with decimal salt as No. 1, deducting the silver added.

The Standard Solutions and Apparatus.

(*a*) **Standard Salt Solution.**—Pure sodium chloride is readily purchased. It is made by passing HCl gas into a strong solution of common salt, when pure sodium chloride crystallizes out. The crystals are slightly washed with cold water, dried, and heated to dull redness. When cold, 5·419 gm. are weighed and dissolved in 1 litre of distilled water at 15° C. 100 c.c. of this solution will precipitate exactly 1 gm. of silver. It is preserved in a well-stoppered bottle, and shaken before use.

(*b*) **Decimal Salt Solution.**—100 c.c. of the above solution are diluted to exactly 1 litre with distilled water at 15° C. 1 c.c. will precipitate 0·001 gm. of silver.

(*c*) **Decimal Silver Solution.**—Pure metallic silver is best prepared by galvanic action from pure chloride; and as clean and safe a method as any is to wrap a lump of clean zinc, into which a silver wire is melted, with a piece of wetted bladder or calico, so as to keep any particles of impurity contained in the zinc from the silver. The chloride is placed at the bottom of a porcelain dish, covered with dilute sulphuric acid, and the zinc laid in the middle; the silver wire is bent over so as to be immersed in the chloride. As soon as the acid begins to act upon the zinc the reduction of the chloride commences, and proceeds gradually throughout the mass; the resulting finely-divided silver is well-washed, first with dilute acid, then with hot water, till all acid and soluble zinc salts are removed.

The moist metal is then mixed with a little sodium carbonate, saltpetre, and borax, say about an eighth part of each, dried perfectly, then melted. **Mulder** recommends that the melting should be done in a porcelain crucible immersed in sand contained in a common earthen crucible; borax is sprinkled over the surface of the sand so that it may be somewhat vitrified, that in pouring out the silver when melted no particles of dirt or sand may fall into it. If the quantity of metal be small it may be melted in a porcelain crucible over a gas blowpipe.

The molten metal obtained in either case can be poured into cold water and so granulated, or upon a slab of pipe clay, into which a glass plate has been pressed when soft so as to form a shallow mould. The metal is then washed well with boiling water to remove accidental surface impurities, and rolled into thin strips by a goldsmith's mill, in order that it may readily be cut for weighing. The granulated metal is, of course, ready for use at once without any rolling.

1 gm. of this silver is dissolved in pure dilute nitric acid, and diluted to 1 litre; each c.c. contains 0·001 gm. of silver. It should be kept from the light.

(*d*) **Dropping Apparatus for Concluding the Assay.**—Mulder constructs a special apparatus for this purpose consisting of a pear-shaped vessel fixed in a stand, with special arrangements for preventing any continued flow of liquid. The delivery tube has an opening of such size that 20 drops measure exactly 1 c.c. The vessel itself is not graduated. As this arrangement is of more service in assay than in general laboratories, it need not be further described here. A small burette divided in $\frac{1}{10}$ c.c. with a convenient dropping tube will answer every purpose, and possesses the further advantage of recording the actual volume of fluid delivered.

The 100 c.c. pipette, for delivering the concentrated salt solution, must be accurately graduated, and should deliver exactly 100 gm. of distilled water at 15° C.

The test bottles, holding about 200 c.c., should have their stoppers well ground and brought to a point, and should be fitted into japanned tin tubes reaching as high as the neck, so as to preserve the precipitated chloride from the action of light, and, when shaken, a piece of black cloth should be placed over the stopper.

(*e*) **Titration of the Standard Salt Solution.**—From what has previously been stated as to the principle of this method, it will be seen that it is not possible to rely absolutely upon a standard solution of salt containing 5·419 gm. per litre, although this is chemically correct in its strength. The real working value must be found by experiment. From 1·002 to 1·004 gm. of absolutely pure silver is weighed on the assay balance, put into a test bottle with about 5 c.c. of pure nitric acid of about 1·2 sp. gr., gently heated in the water or sand bath till it is all dissolved. The nitrous vapours are then blown from the bottle, and it is set aside to cool down to about 16° C. or 60° Fahr.

The 100 c.c. pipette, which should be securely fixed in a support, is then carefully filled with the salt solution, and delivered into the test bottle contained in its case, the moistened stopper inserted, covered over with the black velvet or cloth, and shaken continuously till the chloride has clotted and the liquid become clear; the stopper is then slightly lifted, and its point touched against the neck of the bottle to remove excess of liquid, again inserted, and any particles of chloride washed down from the top of the bottle by carefully shaking the clear liquid over them. The bottle is then brought under the decimal salt burette, and ½ c.c. added, the mixture shaken, cleared, another ½ c.c. put in and the bottle lifted partly out of its case to see if the precipitate is considerable; lastly, 2 or 3 drops only of the solution are added at a time until no further opacity is produced by the final drop. Suppose, for instance, that in titrating the salt solution it is found that 1·003 gm. of silver require 100 c.c. concentrated, and 4 c.c. decimal solution, altogether equal to 100·4 c.c. concentrated, then—

$$1{\cdot}003 \text{ silver} : 1{\cdot}000 :: 100{\cdot}4 \text{ salt} : x. \qquad x = 100{\cdot}0999.$$

The result is within $\frac{1}{10000}$ of 100·1, which is near enough for the purpose, and may be more conveniently used. The operator therefore knows that 100·1 c.c. of the concentrated salt solution at 15° C. will exactly precipitate 1 gm. silver, and in his examination of alloys calculates accordingly.

In the assay of coin and plate of the English standard, namely, 11·1 silver and 0·9 copper, the weight corresponding to 1 gm. of silver is 1·081 gm. therefore in examining this alloy 1·085 gm. may be weighed.

When the quantity of silver is not approximately known, a preliminary analysis is necessary, which is best made by dissolving $\frac{1}{2}$ or 1 gm. of the alloy in nitric acid, and precipitating very carefully with the concentrated salt solution from a $\frac{1}{10}$ c.c. burette. Suppose that in this manner 1 gm. of alloy required 45 c.c. salt solution,

salt salt silver silver
100·1 : 45 : : 1 : x
x = 0·4495
And 0·4495 : 1·003 : : 1 : x
x = 2·231.

2·231 gm. of this particular alloy are therefore taken for the assay.

Where alloys of silver contain sulphur or gold, with small quantities of tin, lead, or antimony, they are first treated with a small quantity of nitric acid so long as red vapours are disengaged, then boiled with concentrated sulphuric acid till the gold has become compact, set aside to cool, diluted with water, and titrated as above.

SULPHUR.

S = 32·06.

Determination in Pyrites, Ores, Residues, etc.

1. Alkalimetric Method (Pelouze).

THIS process, designed for the rapid determination of sulphur in iron and copper pyrites, has hitherto been thought tolerably accurate, but experience has shown that it cannot be relied upon except for rough technical purposes.

The process is based on the fact that when a sulphide is ignited with potassium chlorate and sodium carbonate the sulphur is converted entirely into sulphuric acid, which expels its equivalent proportion of carbonic acid from the soda, forming neutral sodium sulphate; if, therefore, an accurately weighed quantity of the substance be fused with a known weight of pure sodium carbonate in excess, and the resulting mass titrated with normal acid in order to find the quantity of unaltered carbonate, the proportion of sulphur is readily calculated from the difference between the volume of normal acid required to saturate the original carbonate and that actually required after the ignition.

It is advisable to take 1 gm. of the finely levigated pyrites and 5·3 gm. of pure sodium carbonate for each assay; and as 5·3 gm. of sodium carbonate represent 100 c.c. of normal sulphuric acid, it is only necessary to subtract the number of c.c. used after the ignition from 100, and multiply the remainder by 0·016, in order to arrive at the weight of sulphur in the 1 gm. of pyrites, and by moving the decimal point two places to the right the percentage is obtained.

EXAMPLE: 1 gm. of finely ground FeS_2 was mixed *intimately* with 5·3 gm. sodium carbonate, and about 7 gm. each of potassium chlorate and decrepitated sodium chloride in powder; then introduced into a platinum crucible, and gradually exposed to a dull red heat for 10 minutes; the crucible allowed to cool, and warm water added; the solution so obtained was brought on a moistened filter, the residue emptied into a beaker and boiled with a large quantity of water, brought on the filter, and washed with boiling water till all soluble matter was removed; the filtrate coloured with methyl orange, and titrated. 67 c.c. of normal acid were required, which deducted from 100, left 33 c.c.; this multiplied by 0·016 gave 0·528 gm. or 52·8 per cent. S.

Burnt Pyrites.—The only satisfactory volumetric method of determining the sulphur in the residual ores of pyrites is that described by Watson,[1] which is in daily use in large alkali works. In order to avoid calculation, Watson adopts the following method:—

Standard hydrochloric acid.—1 c.c. = 0·02 gm. Na_2O.

Sodium bicarbonate.—This may be the ordinary commercial salt, but its exact alkalinity must be ascertained by the standard acid. Where a number of analyses are being made, a good quantity of the salt should be well mixed, and kept in a stoppered bottle. Its exact alkalinity having been once determined it will not alter, though daily opened.

METHOD OF PROCEDURE: 2 gm. of bicarbonate are placed in a crucible which may be either of platinum, porcelain, or nickel, and to it is added 5·16 gm. of the finely powdered ore, then intimately mixed with a flattened glass rod. Heat gently over a Bunsen burner for 5 or 10 minutes, and break up the mass with a stout copper wire. After stirring, the heat is increased and continued for 10 or 15 minutes. The crucible is then washed out with hot water into a beaker. The mixture is boiled for 15 minutes, filtered into a flask, the residue washed repeatedly with hot water, then cooled and titrated with the standard acid, using methyl orange as indicator.

EXAMPLE 2 gm. of the bicarbonate originally required 37·5 c.c. of acid. After ignition with the ore, 28 c.c. were required. The difference = 9·5 c.c., divided by 5 will give 1·9, which is the percentage of total sulphur in the ore.

This total sulphur includes that which exists as soluble sulphide, and which is not available for acid making. In order to find the amount of this soluble sulphur, Watson boils 5·16 gm. of the ore with 5 c.c. of standard sodium carbonate (1 c.c. = 0·05 gm. Na_2O) diluted with water, for 15 minutes. After filtering and washing, the filtrate is titrated with the standard hydrochloric acid, and the difference between the volume used and that which was originally required for 5 c.c. of the soda solution is divided by 5, as in the case of the former process, which gives at once the percentage of sulphur existing in the ore in a soluble form. The results are not absolutely exact, but quite near enough to guide a manufacturer in the working of the furnaces.

This method is not available for unburnt pyrites.

2. Determination of Sulphur in Coal Gas.

A most convenient and accurate process for this determination is that of Wildenstein (see p. 337). The liquid produced by burning the measured gas in a Letheby or Vernon Harcourt apparatus is well mixed, and brought to a definite volume; a portion representing a known number of cubic feet of gas is then poured into a glass, porcelain, or platinum basin, acidified slightly with HCl, heated to boiling, and a measured excess of standard barium chloride added; the excess of acid is then cautiously neutralized with ammonia (free from carbonate), and the excess of barium ascertained by standard potassium chromate exactly as described on p. 337.

---

[1] *J. S. C. I.*, 1888, 7, 305.

The usual method of stating results is in grains of sulphur per 100 cubic feet of gas. This may be done very readily by using semi-normal solutions of barium chloride and potassium chromate on the metric system, and multiplying the number of c.c. of barium solution required by the factor 0·1234, which at once gives the amount of sulphur in grains.

3. Determination of Sulphur in Sulphides decomposable by Hydrochloric or Sulphuric Acid (Weil).

This process communicated to me by M. Weil, is based on the fact that, in the case of sulphides where the whole of the sulphur is given off as H_2S by heating with HCl or H_2SO_4, the H_2S may be evolved into an excess of a standard alkaline copper solution. After the action is complete, the amount of Cu left unreduced is determined by standard stannous chloride. The method is available for the sulphides of lead, antimony, zinc, iron, etc. Operators should consult and practise the methods described on p. 209, in order to become accustomed to the special reaction involved.

Method of Procedure: From 1 to 10 gm. of material (according to its richness in sulphur) in the finest state of division, are put into a long-necked flask of about 200 c.c. capacity, to which is fitted a bent delivery tube, so arranged as to dip to the bottom of a tall cylinder, containing 50 or 100 c.c. of standard copper solution made by dissolving 39·283 gm. of cupric sulphate, 200 gm. of Rochelle salt, and 125 gm. of pure caustic soda in water, and diluting to 1 litre (10 c.c. = 0·1 gm. Cu). When this is ready, a few pieces of granulated zinc are added to the sulphide. 75 c.c. of strong HCl are then poured over them, the cork with delivery tube immediately inserted, connected with the copper solution, and the flask heated on a sand-bath until all evolution of H_2S is ended. The blue solution and black precipitate are then brought on a filter, filtrate and washings collected in a 200 or 250 c.c. flask, and diluted to the mark; 20 c.c. of the clear blue liquid are then measured into a boiling flask, and evaporated to 10 or 15 c.c. 25 to 50 c.c. of strong HCl are then added, and the standard tin solution dropped in while boiling, until the blue gives place to a clear pure yellow.

Each c.c. of standard copper solution represents 0·005043 gm. of sulphur or 1 gm. of copper (= 100 c.c. of solution) = 0·5043 gm. of sulphur. The addition of the granulated zinc facilitates the liberation of the H_2S, and sweeps it out of the flask; moreover, in the case of dealing with lead sulphide, which forms insoluble lead chloride, it materially assists the decomposition. Alkaline tartrate solution of copper may be used in place of ammoniacal solution if so desired.

EXAMPLES (Weil): 1 gm. of galena was taken, and the gas delivered into 50 c.c. of standard copper solution (= 0·5 gm. Cu). After complete precipitation the blue liquid was diluted to 200 c.c. 20 c.c. of this required 12·5 c.c. of stannous chloride, the titre of which was 16·5 c.c. for 0·04 gm. Cu. Therefore 16·5 : 0·04 : : 12·5 . 0·0303. Thus 200 c.c (= 1 gm. galena) represent 0·303 gm. Cu. Then 0·5 gm. Cu, less 0·303 = 0·197 gm. Cu for 1 gm. galena or 19·7 for 100 gm. Consequently 19·7 × 0·5043 = 9·94 per cent. S. Determination by weight gave 9·85 per cent. Again, 1 gm. zinc sulphide was taken with 100 c.c. copper solution and made up to 250 c.c., 25 c.c. of which required 14·3 c.c. of same stannous chloride, or 143 c.c. for the 1 gm. sulphide. This represents 0·347 gm. Cu. Thus 1 - 0·347 = 0·653 gm. Cu (precipitated as CuS) or 65·3 per 100. Consequently, 65·3 × 0·5043 = 32·9 per cent. S. Control determination by weight gave 33 per cent.

The process has given me good technical results with Sb_2S_3, but the proportion of sulphur to copper is too great to expect strict accuracy.

4. Determination of Alkali Sulphides by Standard Zinc Solution.

This method, which is simply the converse of that described under Zinc, is especially applicable for the technical determination of alkali sulphides in impure alkalis, mother-liquors, etc.

If the zinc solution be made by dissolving 3·268 gm. of pure metallic zinc in hydrochloric acid, supersaturating with ammonia, and diluting to 1 litre, 1 c.c. will respectively indicate—

0·0016	gm. Sulphur
0·0039	„ Sodium sulphide
0·00551	„ Potassium sulphide
0·0034	„ Ammonium sulphide $(NH_4)_2S$

The zinc solution is added from a burette until no dark colour is shown when a drop is brought in contact with solution of nickel sulphate spread in drops on a white porcelain tile.

5. Sulphurous Acid and Sulphites.

The difficulties formerly presented in the iodimetric analysis of these substances are now fortunately quite overcome by the modification devised by Giles and Shearer.[1] A valuable series of experiments on the determination of SO_2, either free or combined, is detailed in these papers. The modification is both simple and exact, and consists in adding the weighed SO_2 or the sulphite in powder to a measured excess of $^N/_{10}$ iodine without dilution with water, and when the decomposition is complete, titrating back with $^N/_{10}$ thiosulphate. Very concentrated solutions of SO_2 are cooled by a freezing mixture, and enclosed in thin bulbs, which can be broken under the iodine solution : this is, however, not required with the ordinary preparations. Sulphites and bisulphites of the alkalis and alkaline earths, also of zinc and aluminium, may all be titrated in this way with accuracy ; the less soluble salts, of course, requiring more time and agitation to ensure their decomposition. A preliminary titration is first made with a considerable excess of iodine, and a second with a more moderate excess as indicated by the first trial.

---

[1] *J. S. C. I.*, 1884, **3**, 197 *and* 1885, **4**, 303.

1 c.c. $^{N}/_{10}$ iodine = 0·0032035 gm. SO_2.

The authors found that when perfectly pure iodine and neutral potassium iodide were used for the standard solution, its strength remained intact for a long period; and the same with the thiosulphate, if the addition of about 2 gm. of potassium bicarbonate to the litre was made, and the stock solution kept in the dark.

From a large number of experiments they also deduced the simple law of the ratio between any given percentage of SO_2 in aqueous solution at 15·4° and 760 mm., and the specific gravity; namely, the percentage found by titration multiplied by 0·005 and added to unity gives the sp. gr.

In cases where the iodine method may not be suitable, W. B. Giles recommends the use of a standard solution of ammoniacal silver nitrate. This process is applicable alike to SO_2, sulphites and bisulphites. The silver solution may conveniently be of $^{N}/_{10}$ strength, but before use ammonia is added in sufficient quantity, first to produce a precipitate of silver oxide, then to dissolve it to a clear solution. A known excess of this solution is digested in a closed bottle, with the substance, in a water-bath for some hours, the result of which is the reduction of the silver as a bright mirror on the sides of the vessel. The filtered liquid and washings may then be titrated by thiocyanate for the excess of silver, or the mirror together with any collected on the filter after washing and burning to ash may be dissolved in nitric acid and determined by the same process (p. 150).

1 c.c. $^{N}/_{10}$ silver = 0·0032035 gm. of SO_2.

Example · 0·1974 gm. of chemically pure potassium metabisulphite $K_2S_2O_5$ was weighed out and treated as above described, the mirror of silver and a little on the filter determined gave 0·1918 gm. of metallic silver, which multiplied by the factor 1·028 gives 0·1971 of metabisulphite or 99·9 per cent.

This method is very useful in determining the percentage of the SO_2 in liquefied sulphurous acid. By cooling down this substance to a point at which the vapour tension is but small, small bulbs can be filled with facility and sealed up. After weighing they are introduced into a well-stoppered bottle containing an excess of the ammoniacal silver, and the stopper firmly secured by a clamp. By shaking the bottle vigorously the bulb is broken, and the determination is then conducted as above described.

$$Ag_2ON_2O_5 + SO_2 + xNH_3 = Ag_2 + SO_3 + N_2O_5 + xNH_3.$$

6. Analysis of Mixtures of Alkali Sulphides, Sulphites, Thiosulphates, and Sulphates.

The determination of the above-mentioned substances when existing together in any given solution presents great difficulty. Richardson and Aykroyd[1] have, however, published a method which seems to give fairly accurate results.

---

[1] *J. S. C. I.*, 1896, **15**, 171.

The determination of the SO_3 in such a mixture cannot be done volumetrically, but by the addition of about 5 gm. of tartaric acid to such a quantity of solution of mixed thiosulphate, sulphate, and sulphite as would be usually taken for analysis, the SO_3 may be precipitated with barium chloride in the cold. The precipitate of $BaSO_4$ contains some barium sulphite, but this is easily removed by hot dilute HCl and boiling water. The thiosulphate produces no SO_3 whatever in these circumstances, whereas in the presence of a mineral acid, sulphate is always produced.

The sulphides are determined by standard ammoniacal zinc solution (see 4, p. 327), which is of such strength that 1 c.c. = 0·0016 gm. of S, using nickel sulphate solution as an external indicator.

The zinc solution is also used for removing sulphides from a mixture of these with thiosulphates, sulphites, and sulphates prior to the determination of the latter bodies. In this case it is only necessary to add a slight excess of the zinc solution, and filter off the precipitated sulphide.

The authors of this method, after pointing out the value of Giles and Shearer's method of determining sulphites by iodine just described, mention a method devised by themselves, which enables them to determine not only sulphites but free SO_2, not only in a pure state but in mixtures with sulphates, thiosulphates, and sulphides. They avail themselves of the well-known reaction that when iodine is added to a neutral sulphite, neutral sulphate and an equivalent amount of hydriodic acid are formed.

$$Na_2SO_3 + I_2 + H_2O = Na_2SO_4 + 2HI,$$

and the acidity of the solution may be accurately measured by standard alkali and methyl orange.

The authors state that the best plan is to convert all sulphites to bisulphites, i.e. to the hydrogen sulphite of the base: this is necessary because a sulphite may be alkaline or it may be exclusively acid. Sodium bisulphite is quite neutral to methyl orange, and by titrating the solution of a neutral sulphite with $^N/_{10}$ sulphuric acid, using methyl orange, a point is reached when all the sulphite is converted into the acid sulphite. The reason for this is patent when the reaction which takes place when an acid sulphite acts upon iodine is considered—

$$NaHSO_3 + OH_2 + I_2 = NaHSO_4 + 2HI.$$

Here is a new factor, inasmuch as the titration with alkali and with methyl orange as indicator is concerned; although the acid sodium sulphite is neutral to methyl orange, the acid sodium sulphate is acid to the full and exact extent of its combining power.

Thus one molecule of sodium bisulphite, on titration with $^N/_{10}$ iodine, liberates acid equivalent to three molecules of sodium or potassium hydrate.

Example: A solution containing 1·62 per cent. of $Na_2SO_3 . 7Aq$ was titrated. Iodine solution equivalent to 9·5 c.c. $^N/_{10}$ I; 29·9 c.c. were required; the mixture required 14·6 c.c. of $^N/_{10}$ NaHO. Now 9·5 c.c. $^N/_{10}$ I and 14·6 c.c. $^N/_{10}$ NaHO are in the ratio of 2: 3 almost exactly; by using 0·0126 as the factor for the c.c. of $^N/_{10}$ I and 0·084 for the $^N/_{10}$ NaHO, both results give 1·64 per cent. of $Na_2SO_3 . 7Aq$. (Of course the sulphite solution had been previously titrated with $^N/_{10}$ H_2SO_4 in the presence of methyl orange.)

As the details of calculation may be somewhat obscure to those who have not experimented in this direction, the working out of an actual analysis is of interest. A solution containing one per cent. of pure sodium thiosulphate, and 0·78 per cent. of sodium sulphite, was titrated upon 20 c.c. of iodine; 19·3 c.c. were required to decolorise; to neutralise with methyl orange as indicator 17·9 c.c. of $^N/_{10}$ soda were required; therefore 100 c.c. of the mixture required 103·6 c.c. iodine and 92·7 c.c. of $^N/_{10}$ soda respectively; the c.c. of soda × 0·0084 give 0·7787 as the percentage of $Na_2SO_3 . 7Aq$, and this figure ÷ 0·0126 (the factor for 1 c.c. iodine in $Na_2SO_3 . 7Aq$) gives 61·8 c.c., and this subtracted from 103·6 c.c. of total iodine required gives 41·8 c.c., and this × 0·0248 gives 1·036 instead of 1 per cent. of $Na_2S_2O_3 . 5Aq$.

The advantage of this method is better seen in the case of a complex mixture, where one must remove sulphides or other bodies by the addition of an alkaline solution of zinc or other precipitating agent. The alkaline filtrate is speedily brought into a condition suitable for iodimetric and alkalimetric titration by the method proposed.

Example: A solution of known amounts of sodium thiosulphate and sulphite was treated with 10 c.c. of a strongly ammoniacal zinc-chloride solution, and the mixture was titrated with it until it gave a neutral reaction with methyl orange; it was now made to 1000 c.c. and was titrated upon a known volume of $^N/_{10}$ iodine, using starch to find the end-reaction (which is otherwise somewhat obscured by the methyl orange). The disappearance of the blue colour and the appearance of the pinkish-purple of the acidified methyl orange is both interesting and striking. Titration with $^N/_{10}$ NaHO was now easily accomplished. The results were exact in the case of thiosulphate, and very slightly in excess in the case of sulphite.

After the sulphite and thiosulphate solution has been titrated upon a known volume of $^N/_{10}$ iodine, the sulphate formed is determined by barium at a boiling heat in the presence of a little dilute HCl. Any sulphate in the original solution is, of course, determined by the tartaric acid method and deducted from the result. Ammonium tartrate must be avoided in the process, owing to its solvent action on barium sulphate.

The process is only strictly applicable in the absence of organic matter. When that is present it is preferable to use the iodine process as follows:—

(1) *Total Iodine value of solution* = $H_2S + H_2SO_3 + H_2S_2O_3$ determined by running known volume of solution into excess of $^N/_{10}$ iodine acidified with hydrochloric acid and titrating back with $^N/_{10}$ thiosulphate. This gives $A = H_2S + H_2SO_3 + H_2S_2O_3$ accurately without loss.

(2) *Iodine value of* H_2S.—Add excess of ammoniacal zinc chloride, filter, wash; wash ZnS into $^N/_{10}$ iodine and hydrochloric acid (as described on p. 81). This gives $B = H_2S$ accurately. Then A – B gives $H_2SO_3 + H_2S_2O_3$ accurately.

(3) *Iodine value of* $H_2S_2O_3$.—To filtrate from B add acid to neutralize exactly with methyl orange as indicator.

Then titrate with iodine and starch $C = H_2S_2O_3 + H_2SO_3$ *in filtrate*

Then with $^N/_{10}$ alkali ,, $\frac{2}{3}$ alkali $^N/^{10}$ $D = H_2SO_3$,, The $\frac{2}{3}$ N/10 alkali used = iodine equivalent of H_2SO_3 *in the filtrate* (not in the original solution, as oxidation occurs in filtration) accurately.

And $C - D = H_2S_2O_3$ accurately.

(4) *Iodine value of* H_2SO_3.—Got by difference

$$\begin{array}{rcll} H_2SO_3 + H_2S_2O_3 & = & A - B & \text{accurately} \\ H_2S_2O_3 & = & C - D & ,, \\ H_2SO_3 & = & A - B - (C - D) & ,, \end{array}$$

The procedure, so modified, is to obtain the sulphurous acid by difference in place of direct determinations. Thiosulphate suffers no appreciable oxidation on filtration; sulphite does. Hence by determining thiosulphate and sulphide accurately sulphite is got by difference accurately. This difference figure is always rather higher than the one deduced acidimetrically (D, above.)

Another series of processes for ascertaining the proportions of mixtures of sulphuretted hydrogen, sulphurous and thiosulphuric acids has been worked out by W. Feld.[1] The methods described are applicable to the alkali or alkaline earth salts of the above acids, even when present in small quantities.

(1) SULPHIDES.—Alkali or alkaline earth sulphides evolve the whole of their sulphur as H_2S when boiled with a concentrated solution of magnesium chloride in an atmosphere of CO_2. The powdered and moistened sample is placed in a 300 c.c. Erlenmeyer flask provided with a doubly-bored rubber stopper. Through one hole a small tap-funnel passes to the bottom of the flask, through the other a glass tube leads to four sets of potash-bulbs in series. The last of these is connected to a 10 litre bottle acting as aspirator. The neck of the tap-funnel is connected to a supply of CO_2, which must have no action on a solution of iodine. The first set of potash-bulbs is empty, the second and third contain rather more iodine solution than will suffice to absorb all the H_2S evolved, the fourth contains N/10 thiosulphate solution, to take up any iodine carried over by the CO_2. About 1 litre of CO_2 is first passed, in order to displace the air in the apparatus, the tap of the funnel is then closed, and about 20 c.c. of 25 per cent. magnesium chloride solution introduced. Connection is now made to the supply of CO_2, and the magnesium chloride solution run into the flask, the contents of which are slowly heated to boiling in a current of CO_2 passing at the rate of 10 litres in three-quarters of an hour. The operation is usually ended when 5 litres have passed. The contents of the potash-bulbs are finally washed out and titrated; the reactions are—

$$BaS + MgCl_2 + CO_2 + H_2O = BaCl_2 + MgCO_3 + H_2S, \text{ and } H_2S + I_2 = 2HI + S.$$

Test analyses with $BaSH . OH + 5H_2O$ gave good results.

(2) SULPHITES are determined in the same apparatus and in the same way, hydrochloric acid taking the place of magnesium chloride.

(3) THIOSULPHATES evolve some H_2S when treated with hydrochloric acid. The following method is found, however, to give accurate results: The thiosulphate is first converted (by titration with iodine solution)

---

[1] *Die Chem. Ind.* 1898, 372

into tetrathionate. The solution of the tetrathionate, diluted with 50 c.c. of water, is placed in the flask with excess of aluminium foil, and treated, in an atmosphere of CO_2, with *dilute* hydrochloric acid in the cold. The reduction to H_2S, which is collected as before, takes place quantitatively according to the equation

$$Na_2S_4O_6 + 20HCl + 3Al_2 = 2NaCl + 3Al_2Cl_6 + 6H_2O + 4H_2S.$$

(4) THIOSULPHATE IN PRESENCE OF SULPHITE.—This determination is made by method (3). The titration with iodine oxidizes the sulphite into sulphate, which is not affected by nascent hydrogen.

(5) SULPHITE IN PRESENCE OF THIOSULPHATE.—Excess of mercuric chloride is added to the substance; the thiosulphate is thus converted into mercuric sulphide—

$$Na_2S_2O_3 + HgCl_2 + H_2O = Na_2SO_4 + HgS + 2HCl,$$

whilst the sulphite is not affected and is determined by (2).

(6) SULPHIDE, SULPHITE, AND THIOSULPHATE.—The sample is first distilled with magnesium chloride, as described in (1). This gives the sulphide. The potash-bulbs are then refilled, excess of mercuric chloride added to the cold contents of the flask, which are then distilled with hydrochloric acid as described under (2). This gives the sulphite. The thiosulphate is determined in a fresh sample by titrating with iodine, by which the sulphide is oxidized to sulphur and the sulphite to sulphate, and then reducing by nascent hydrogen as described under (3).

When, in addition to the alkali or alkaline earth salts of the acids considered, the substance contains polysulphides, free sulphur, and sulphides of the heavy metals, the difficulties are much greater. In such a case satisfactory results may be obtained as follows: Free sulphur is extracted by carbon disulphide, and weighed after evaporation of the solvent. The sulphur present as sulphide is then determined by method (1). In this operation the sulphur of the polysulphides is evolved partly as H_2S, the remainder separating in the free state. The latter part is extracted by carbon disulphide. If a sulphite is present, however, some thiosulphate is formed. The solution is now titrated with iodine, during which operation the sulphur present as ferrous sulphide separates in the free state and is extracted with carbon disulphide. The solution is now treated by method (3) to determine the thiosulphate. The presence of other polythionic acids introduces an error here. In solid substances sulphites may occur in presence of polysulphides; in this case they are determined by treatment with mercuric chloride and distillation with hydrochloric acid, according to method (2).

Determination of Thiosulphate in Presence of Sulphide, Sulphite, and Bisulphite. A. Sander.[1]

Determination of Thiosulphate in Presence of Sulphide.—This is done by precipitation with mercuric chloride, each molecule of the thiosulphate liberating 2 molecules of HCl, which can be titrated.

$$2Na_2S_2O_3 + 3HgCl_2 + 2H_2O = 2Na_2SO_4 + 4HCl + 2HgS . HgCl_2$$
$$\text{and } 2Na_2S + 3HgCl_2 = 4NaCl + 2HgS . HgCl_2.$$

---

[1] *Chem. Zeit.*, 1915, **39**, 945.

The total of thiosulphate and sulphide is first found by titration with iodine solution. A second portion is treated with excess of $HgCl_2$, shaken until the dark precipitate has become a pure white, then NH_4Cl is added (to prevent the precipitation of mercuric oxide by the alkali), and the cloudy liquid titrated with $^N/_{10}$ NaOH, using methyl orange as indicator. The alkali consumed, divided by 2, gives the iodine consumption of the thiosulphate alone, and the difference between this and the first titration gives the iodine consumed by the sulphide.

Determination of Thiosulphate in Presence of Sulphite.—Bosshard and Grob's[1] method is recommended, in which the sulphite is first titrated with standard HCl, using M.O. as indicator, thus

$$Na_2SO_3 + HCl = NaHSO_3 + NaCl.$$

To the resulting liquid 1 gm. of NaCl and 300 c.c. of a saturated solution of $HgCl_2$ are added and the acid set free is titrated with standard NaOH solution in presence of phenolphthalein, the reaction being as follows:—

$$NaHSO_3 + HgCl_2 = HgCl . SO_3Na + HCl$$

(sodium chloride is added to counteract the tendency of the mercuric chloride to become partially hydrolysed and react acid).

Determination of Thiosulphate, Sulphide and Sulphite in the same Solution. This can be carried out accurately in less than 10 minutes by the following method.

(1) 10 to 20 c.c. of the solution are run into a measured excess of $^N/_{10}$ iodine solution acidified with 5 to 10 c.c. $^N/_{10}$ HCl, and the excess of iodine titrated with $^N/_{10}$ thiosulphate. This gives the total of thiosulphate, sulphide and sulphite [x].

(2) The hydriodic acid liberated by the sulphite in (1) is directly titrated with caustic soda and 1 or 2 drops of M.O. On subtracting the value of the acid introduced in (1), the iodine value of the sulphite is obtained [y].

(3) The iodine value of the thiosulphate [z] is found with mercuric chloride as above, and the sulphide is then deduced by subtraction,

$$\left[x - \left(y + \frac{z}{2}\right)\right].$$

7. Sulphur in Steel (and Sulphides) by Oxidation to Sulphate.[2]

Sulphur in steels is determined as follows: 5 gm. of steel are placed in a flask through which hydrogen may be passed and which is connected with a 10-bulb tube for absorption of the hydrogen sulphide. The absorption bulbs contain 6 to 7 gm. of sodium hydroxide in 50 to 60 c.c. of water. Air is removed from the apparatus by hydrogen and 100 c.c. of hydrochloric acid (sp. gr. 1.1) added. After the reaction has moderated the solution is heated just to boiling for 5 minutes after the steel has dissolved. The contents of the bulbs are washed, with as little water as possible, into a flask containing 10 c.c. of 0·3N sodium hypobromite in 2·5N sodium hydroxide or 10 c.c.. of 0·3N sodium hypochlorite in 4N sodium hydroxide, and allowed to stand for 3 to 4 minutes, then 2 to 3 gm. of potassium iodide are added, the solution diluted to 150 c.c., neutralized with concentrated hydrochloric acid and 5 c.c. excess acid added. It is then titrated with $^N/_{10}$ sodium thiosulphate. Sulphides which are soluble in hydrochloric acid are determined in the same way. Insoluble sulphides are ignited with powdered iron in an atmosphere of hydrogen or carbon dioxide, thus producing ferrous sulphide. The determination is then completed as above. The method is accurate to within about 0·1 per cent.

---

[1] *Chem. Zeit.*, 1913, **37**, 465.

[2] Willard and Cake, *J. A. C. S.*, 1921, **43**, 1610.

For determination of sulphur in steel by evolution methods, see p. 250.

SULPHURETTED HYDROGEN.

H_2S = 34·076.

1 c.c. $^N/_{10}$ arsenious solution = 0·0025557 gm. H_2S.

1. By Arsenious Acid (Mohr).

THIS residual process is far preferable to the direct titration of sulphuretted hydrogen by iodine. It is based on the precipitation of arsenious sulphide from a hydrochloric acid solution of arsenic trioxide by sulphuretted hydrogen. The following reaction takes place—

$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O$$

from which we see that 197·92 gm. of arsenic trioxide are equivalent to 102·228 gm. of sulphuretted hydrogen. Hence, 4·948 gm. of As_2O_3 (= 1 litre of $^N/_{10}$ arsenious solution) = 2·5557 gm. of H_2S, or 1 c.c. $^N/_{10}$ arsenious solution = 0·0025557 gm. H_2S.

The excess of arsenious acid is found by $^N/_{10}$ iodine and starch, as on p. 144. In determining the strength of sulphuretted hydrogen water the following plan may be pursued.

METHOD OF PROCEDURE: A measured quantity, say 10 c.c. of $^N/_{10}$ arsenious solution is put into a 300 c.c. flask, and 20 c.c. of sulphuretted hydrogen water added, well mixed, and sufficient HCl added to produce a distinct acid reaction; this produces a precipitate of arsenic sulphide, and the liquid itself is colourless. The whole is then diluted to 300 c.c., filtered through a dry filter into a dry vessel, 100 c.c. of the filtrate taken out and neutralized with sodium bicarbonate, then titrated with $^N/_{10}$ iodine and starch. The quantity of arsenious acid so found is deducted from the original 10 c.c., and the remainder multiplied by the requisite factor for H_2S.

The determination of H_2S contained in coal gas may by this method be made very accurately by leading the gas very slowly through the arsenious solution, or still better, through a dilute solution of caustic alkali, then adding arsenious solution, and titrating as before described. The apparatus devised by Mohr for this purpose is arranged as follows:—

The gas from a common burner is led by means of a vulcanized rubber tube into two successive small wash-bottles containing the alkaline solution; from the last of these it is led into a large Woulfe's bottle filled with water. The bottle has two necks, and a tap at the bottom; one of the necks contains the cork through which the tube carrying the gas is passed; the other, a cork through which a good-sized funnel with a tube reaching to the bottom of the bottle is passed. When the gas begins to bubble through the flask, the tap is opened so as to allow the water to drop rapidly; if the pressure of gas is strong, the funnel tube acts as a safety valve, and allows the water to rise up into the cup of the funnel. When a sufficient quantity of gas has passed into the bottle, say 6 or 8 pints, the water which has issued from the tap into some convenient vessel is measured in cubic inches or litres, and gives the quantity of gas which has displaced it. In order to ensure accurate measurement, all parts of the apparatus must be tight.

The flasks are then separated, and into the second 5 c.c. of arsenious solution are placed, and acidified slightly with HCl. If any traces of a precipitate occur it is set aside for titration with the contents of the first flask, into which 10 c.c or so of arsenious solution are put, acidified as before, both mixed together, diluted to a given measure, filtered, and a measured quantity titrated as before described.

This method does not answer for very crude gas containing large quantities of H_2S unless the absorbing surface is largely increased.

2. By Permanganate (Mohr).

If a solution of H_2S is added to a dilute solution of ferric sulphate, the ferric salt is reduced to the ferrous state, and free sulphur separates. The ferrous salt so produced may be measured accurately by permanganate without removing the separated sulphur. Ferric sulphate, free from ferrous compounds, in sulphuric acid solution, is placed in a stoppered flask, and the solution of H_2S added to it with a pipette; the mixture is allowed to stand half an hour or so, then diluted considerably, and permanganate added until the rose colour appears.

$$55{\cdot}84\ \text{Fe} = 17{\cdot}038\ H_2S$$

or each c.c. of $^{N}/_{10}$ permanganate represents 0·0017038 gm. of H_2S. The process is considerably hastened by placing the stoppered flask containing the acid ferric solution into hot water previous to the addition of H_2S, and excluding air as much as possible.

3. By Iodine.

Sulphuretted hydrogen in mineral waters may be accurately determined by iodine in the following manner:—

Method of Procedure: 10 c.c. or any other necessary volume of $^{N}/_{100}$ iodine solution are measured into a 500 c.c. flask, and the water to be examined added until the colour disappears. 5 c.c. of starch indicator are then added, and $^{N}/_{100}$ iodine until the blue colour appears; the flask is then filled to the mark with pure distilled water. The respective volumes of iodine and starch solution, together with the added water, deducted from the 500 c.c., will show the volume of water actually titrated by the iodine. A correction should be made for the excess of iodine necessary to produce the blue colour.

Fresenius[1] examined the sulphur water of the Grindbrunnen, in Frankfurt a. M., both volumetrically and gravimetrically for H_2S with very concordant results. 361·44 gm. of water (correction for blue colour being allowed) required 20·14 c.c. of iodine, 20·52 c.c. of which contained 0·02527 gm. of free iodine = H_2S 0·0092 gm. per million. 444·65 gm. of the same water required, under the same conditions, 25·05 c.c. of the same iodine solution = H_2S 0·0092 gm. per million. Gravimetrically the H_2S was found to be 0·0094 gm. per million.

SULPHURIC ACID AND SULPHATES.

Monohydrated Sulphuric Acid.

H_2SO_4 = 98·076.

Sulphuric Anhydride.

SO_3 = 80·06.

1. Mohr's Method.

In my opinion the determination of sulphuric acid in most cases is more easily obtained by gravimetric than by volumetric methods, but there are circumstances in which the latter are useful. The indirect process devised by C. Mohr[2] consists in adding a known volume of barium solution to the compound, more than sufficient to precipitate the SO_3. The excess of barium is converted into carbonate, and titrated with normal acid and alkali.

Normal barium chloride is made by dissolving 122·161 gm. of the pure crystals in the litre; this solution likewise suffices for the determination of SO_3 by the direct method.

METHOD OF PROCEDURE: If the substance contains a considerable quantity of free acid, it must be brought nearly to neutrality by adding pure sodium carbonate; if alkaline, slightly acidified with hydrochloric acid; a round number of c.c. of barium solution in excess is then added, and the whole digested in a warm place for some minutes; the excess of barium is precipitated by a mixture of carbonate and caustic ammonia in slight excess; if a piece of litmus paper be thrown into the mixture, a great excess may readily be avoided. The precipitate containing both sulphate and carbonate is now to be collected on a filter, thoroughly washed with boiling water, and titrated.

The difference between the number of c.c. of barium solution added and that of normal acid required for the carbonate will be the measure of the sulphuric acid present; each c.c. of barium solution = 0·04003 gm. SO_3.

EXAMPLE: 2 gm. of pure and dry barium nitrate and 1 gm. of pure potassium sulphate were dissolved separately, mixed, and precipitated hot with carbonate

---

[1] *Z. a. C.* 1875, **14**, 321.

[2] *Ann. der. Chem. u. Pharm.* **90**, 165.

and free ammonia; the precipitate, after being thoroughly washed, gave 1·002 gm. potassium sulphate, instead of 1 gm.

For technical purposes this process may be considerably shortened by the following modification, which dispenses with the washing of the precipitate.

The solution containing the sulphates or sulphuric acid is first rendered neutral; normal barium chloride is then added in excess, then normal sodium carbonate in excess of the barium chloride, and the volume of both solutions noted; the liquid is then made up to 200 or 300 c.c. in a flask, and an aliquot portion filtered off and titrated with normal acid. The difference between the barium chloride and sodium carbonate gives the sulphuric acid.

The solution must of course contain no substance precipitable by sodium carbonate except barium (or, if so, it must be previously removed); nor must it contain any substance precipitable by barium, such as phosphoric or oxalic acid, etc.

2. Titration by Barium Chloride and Potassium Chromate (Wildenstein).

To the hot solution containing the SO_3 to be determined (which must be neutral – or if acid, neutralized with ammonia free from carbonate), a standard solution of barium chloride is added in slight excess, then a solution of potassium chromate of known strength is cautiously added to precipitate the excess of barium. So long as any barium remains in excess, the supernatant liquid is colourless; when it is all precipitated the liquid is yellow, from the potassium chromate; a few drops only of the chromate solution are necessary to produce a distinct colour.

Wildenstein uses a barium solution, of which 1 c.c. = 0·015 gm. SO_3, and chromate 1 c.c. = 0·010 gm. of SO_3. I prefer to use $^N/_2$ solutions, so that 1 c.c. of each is equal to 0·02 gm. of SO_3. If the chromate solution is made of equal value to the barium chloride, the operator has simply to deduct the one from the other, in order to obtain the quantity of barium solution really required to precipitate all the SO_3.

METHOD OF PROCEDURE. The substance or solution containing SO_3 is brought into a small flask, diluted to about 50 c.c., acidified if necessary with HCl, heated to boiling, and precipitated with a slight excess of standard barium chloride delivered from the burette. As the precipitate rapidly settles from a boiling solution, it is easy to avoid any great excess of barium, which would prevent the liquid from clearing so speedily. The mixture is then cautiously neutralized with ammonia free from carbonic acid (to be certain of this, it is well to add to it 2 or 3 drops of calcium chloride or acetate solution).

The flask is then heated to boiling, and the chromate solution added in ½ c.c. or so, each time removing the flask from the heat and allowing to settle until the liquid is of a light yellow colour; the quantity of chromate is then deducted from the barium solution, and the remainder calculated to SO_3.

Or the mixture with barium in excess may be diluted to 100 or 150 c.c., the precipitate allowed to settle thoroughly, and 25 or 50 c.c. of the clear liquid heated to boiling, after neutralizing, and precipitated with chromate until all the barium is carried down as chromate, leaving the liquid of a light yellow colour; the analysis should be checked by a second titration. The process has yielded me very satisfactory results in comparison with the gravimetric barium method; it is peculiarly adapted for determining sulphur in gas when burnt in the Letheby sulphur apparatus, details of which will be found on p. 325.

The presence of alkali and alkaline earthy salts is of no consequence—Zn and Cd do not interfere—Ni, Co, and Cu give coloured solutions which prevent the yellow chromate being seen, but this difficulty can be overcome by the use of an external indicator for showing the excess of chromate. This indicator is an ammoniacal lead solution, made by mixing together, at the time required, one volume of pure ammonia and four volumes of lead acetate solution (1:20). The liquid has an opalescent appearance. To use the indicator, a large drop is spread upon a white porcelain plate, and 1 or 2 drops of the liquid under titration added; if the reddish-yellow colour of lead chromate is produced, there is an excess of chromate, which can be cautiously reduced by adding more barium until the exact balance is reached.

A variation of the chromate method has been devised by Andrews,[1] which is especially serviceable for determining the combined SO_3 in alkali salts. The method is strongly recommended by Reuter[2] as simple and easy of execution.

METHOD OF PROCEDURE. 3 or 4 gm. of pure precipitated barium chromate are dissolved in 30 c.c. of strong hydrochloric acid, and the whole is diluted to 1 litre The liquid to be tested, which should contain about 0·07 gm of SO_3 as an alkali sulphate, is mixed at the boiling point with an excess (150 c.c.) of the chromate solution; the acid is neutralized with pure powdered chalk, and the precipitate is removed by filtration. After thorough cooling, the filtrate is acidified with 5 c.c (not more) of strong HCl, 20 c.c of a 10 per cent. solution of potassium iodide are added, and the liquid is allowed to rest for 5 minutes in a covered beaker and in an atmosphere of carbonic acid (to prevent oxidation of the HI) until the chromic acid is entirely reduced. Finally, it is diluted to 1 or 1½ litre, and titrated quickly with thiosulphate; three atoms of iodine corresponding to 1 molecule of SO_3.

Another variation of the chromate method has been devised by Mitchell and Smith.[3] It consists in using excess of standard ammonium dichromate, and titrating the excess by means of standard ferrous ammonium sulphate.

METHOD OF PROCEDURE: A convenient quantity of a sulphate is taken and dissolved in water or pure hydrochloric acid, or, if necessary, dilute nitric acid, and a slight excess of standard ($^{2N}/_{5}$) solution of barium chloride (48·864 gm. $BaCl_2, H_2O$ per litre) is added. The mixture is boiled and rendered neutral by ammonium hydroxide; sodium acetate, acetic acid, and a slight excess of $^{N}/_{10}$ ammonium dichromate are added. The mixture is made up to 100 c.c, and the precipitate allowed to settle; 25 c.c. of the clear supernatant liquid are titrated with $^{N}/_{20}$ ferrous ammonium sulphate, using potassium ferricyanide as an external indicator, and taking the first appearance of a green tinge as the end-point.

---

[1] *Amer. Chem. Jour.*, 1880, 567

[2] *Chem. Zeit.*, 1898, **22**, 357.

[3] *J. C. S.*, 1909, **95**, 2198.

It should be noted that ammonium dichromate, which is $^{N}/_{10}$ in respect of oxidizing power, is only $^{N}/_{30}$ in respect of precipitating power.

The method appears to be rapid, and the author's results are very accurate.

3. Direct Precipitation with Normal Barium Chloride.

Very good results may be obtained by this method when carefully performed.

METHOD OF PROCEDURE: The substance in solution is to be acidified with hydrochloric acid, heated to boiling, and the barium solution allowed to flow cautiously in from the burette until no further precipitation occurs. The end of the process can only be determined by filtering a portion of the liquid, and testing with a drop of the barium solution. Beale's filter is a good aid in this case. A few drops of clear liquid are poured into a test tube, and a drop of barium solution added from the burette; if a cloudiness appears, the contents of the tubes must be emptied back again, washed out into the liquid, and more barium solution added until all the SO_3 is precipitated. It is advisable to use $^{N}/_{10}$ solution towards the end of the process.

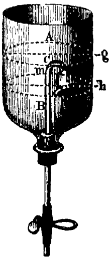

FIG. 48.

Instead of the test tube for finding whether barium or sulphuric acid is in excess, a plate of black glass may be used, on which a drop of the clear solution is placed and tested by either a drop of barium chloride or sodium sulphate—these testing solutions are preferably kept in two small bottles with elongated stoppers. A still better plan is to spot the liquids on a small mirror, as suggested by Haddock;[1] the faintest reaction can then be seen, although the liquid may be highly coloured.

Wildenstein has arranged another method for direct precipitation, especially useful where a constant series of determinations have to be made. The apparatus is shown in fig. 48. A is a bottle of 900 or 1000 c.c. capacity, with the bottom removed, and made of well-annealed glass so as to stand heating; B a thistle funnel bent round, as in the figure, and this siphon filter is put into action by opening the pinch-cock below the cork. The mouth of the funnel is first tied over with a piece of fine cotton cloth, then two thicknesses of Swedish filter-paper, and again with a piece of cotton cloth, the whole being securely tied with waxed thread.

In precipitating SO_3 by barium chloride, there occurs a point similar to the so called neutral point in silver assay, when in one and the same solution both barium and sulphuric acid after a minute or two produce a cloudiness. Owing to this fact, the barium solution must not be reckoned exactly by its amount of $BaCl_2$, but by its working effect; that is to say, the process must be considered ended when the addition of a drop or two of barium solution gives no cloudiness after the lapse of 2 minutes.

---

[1] C. N., 1879, 39, 156.

METHOD OF PROCEDURE: The solution containing the SO_3 having been prepared, and preferably in HCl, the vessel A is filled with warm distilled water and the pinch-cock opened so as to fill the filter to the bend C; the cock is then opened and shut a few times so as to bring the water further down into the tube, but not to fill it entirely; the water is then emptied out of A, and about 400 c.c. of boiled distilled water poured in together with the SO_3 solution, then, if necessary, a small quantity of HCl added, and the barium chloride added in moderate quantity from a burette. After mixing well, and waiting a few minutes a portion is drawn off into a small beaker, and poured back without loss into A; a small quantity is then drawn off into a test tube, and two drops of barium chloride added. So long as a precipitate is produced the liquid is returned to A, and more barium added until a test is taken which shows no distinct cloudiness; the few drops to produce this effect are deducted. If a distinct excess has been used, the analysis must be corrected with a solution of SO_3 corresponding in strength to the barium solution.

A simpler and even more serviceable arrangement of apparatus on the above plan may be made by using as the boiling and precipitating vessel an ordinary beaker standing on wire gauze or a hot plate. The filter is made by taking a small thistle funnel, tied over as described, with about 2 inches of its tube, over which is tightly slipped about 4 or 5 inches of rubber tubing, terminating with a short piece of glass tube drawn out to a small orifice like a pipette; a small pinch-cock is placed across the rubber tube just above the pipette end, so that when hung over the edge of the beaker with the funnel below the surface of the liquid, the apparatus will act as a siphon. It may readily be filled with warm distilled water by gentle suction, then transferred to the liquid under titration. By its means much smaller and more concentrated liquids may be used for the analysis, and consequently a more distinct evidence of the reaction obtained.

4. Determination by Benzidine Hydrochloride.[1]

Benzidine sulphate $C_{12}H_8(NH_2)_2 . H_2SO_4$ is a stable salt almost insoluble in water containing hydrochloric acid Benzidine being a weak organic base, neutral to phenolphthalein, the acid in its sulphate can be titrated with standard alkali. For the determination of sulphuric acid by benzidine Raschig[2] recommends treating the neutral or acid solution of the sulphate with benzidine hydrochloride solution, filtering off the precipitated benzidine sulphate, washing it, and then suspending it in water and titrating the sulphuric acid with $^N/_{10}$ soda.

METHOD OF PROCEDURE: To prepare the solution of benzidine hydrochloride, 6·7 gm. of the free base, or the corresponding amount of the hydrochloride, is rubbed up in a mortar with 20 c.c. of water. The paste is rinsed into a litre flask, 20 c.c. of hydrochloric acid (sp. gr. 1·12) are added, and the solution diluted to the mark. (1 c.c. of this solution corresponds theoretically to 0·00357 gm. H_2SO_4.) The solution has a brown colour and may be filtered if necessary. After some time brown flakes are likely to separate, but these do no harm.

---

[1] See Treadwell's *Analytical Chemistry*, translated by Hall, 2nd edition, Vol. II., p. 658.

[2] *Z. a. C.*, 1903, 42, 617 and 818.

The solution of the sulphate is diluted with water until its volume corresponds to not less than 50 c.c. for each 0·1 gm. of sulphuric acid present. An equal volume of the reagent is added while stirring vigorously. A filter is prepared by placing a perforated porcelain filter plate in a funnel and covering it with two moistened filter papers, one of exactly the same size as the plate and the upper one a little larger. After 10 minutes, the precipitate is filtered off upon this filter, using gentle suction. The last portions of the precipitate are transferred to the filter with the aid of small portions of the clear filtrate, and then the beaker and precipitate are washed with 20 c.c. of cold water, added in several portions. The precipitate and filter, but not the plate, are then transferred to an Erlenmeyer flask, 50 c.c. of water are added and the contents of the stoppered flask shaken until a homogeneous paste is obtained. The rubber stopper is then removed, rinsed with water, a drop of phenolphthalein added, the water heated to about 50° C, and titrated with $^{N}/_{10}$ sodium hydroxide. When the end point is nearly reached, the liquid is boiled for 5 minutes, and the titration then finished.

According to Friedheim and Nydegger,[1] this method gives excellent results in the analysis of all sulphates, provided no substances are present which attack benzidine, and provided the amount of other salts and acids present is not too great. There should not be more than 10 mol. of HCl, 15 mol. HNO_3, 20 mol. $HC_2H_3O_2$, 5 mol. alkali salt, or 2 mol. ferric iron present to 1 mol. H_2SO_4. A satisfactory determination of the sulphur in pyrites may be made by dissolving 0·5 gm. of the sample according to the Lunge method, evaporating off the nitric acid, taking up the residue in a little hydrochloric acid, diluting to 500 c.c and using 100 c.c. for the treatment with benzidine hydrochloride

Hibbard's Modification[2] **(Oxidation of Benzidine Sulphate with Permanganate.**

This is a modification of the method of Raiziss and Dubin.[3] The solution for the precipitation of benzidine sulphate should be free from iron, heavy metals, nitrates, phosphates, and organic matter, and should only contain between 0·5 and 4·0 mgm. SO_4. The liquid (10 to 25 c.c.) is treated with one drop of phenolphthalein and then with dilute sodium hydroxide till just alkaline It is then neutralized with $^{N}/_{10}$ hydrochloric acid and 0·1 c.c. added in excess for each 5 c.c. of solution. Keeping the liquid quite cold, 5 c.c. of 0·8 per cent. benzidine hydrochloride solution is added, and after 15 to 30 minutes the benzidine sulphate is collected in a Gooch crucible, washed with the minimum of cold water, transferred with the asbestos pad to the precipitation flask, and heated with 1 c.c. of 10 per cent. sodium hydroxide solution in a boiling water bath for a few minutes. Then 10 c.c. of dilute sulphuric acid (1 acid : 1 water) is added and hot water to bring the volume to 100 c.c. $^{N}/_{20}$ potassium permanganate is run in until there is 5 c.c. in excess and the solution heated on the water bath for exactly 10 minutes. Then 10 c.c. of $^N/_{20}$ oxalic acid is added and the titration completed with $^N/_{20}$ permanganate. It is advisable to make a blank determination.

---

[1] *Z. a. C.*, 1907, **46**, 9.

[2] *Soil. Sci.*, 1919, **8**, 61.

[3] *J. Biol. Chem.*, 1914, **18**, 297.

1 c.c. $^N/_{20}$ permanganate = 0·12 mgm. SO_4.

PERSULPHATES.

THE alkali persulphates may be readily titrated by adding to their solution a known excess of ferrous salt and determining the amount of oxygen absorbed by titration of the solution with permanganate. The salt, say potassium persulphate, decomposes as follows :—

$$K_2S_2O_8 = K_2SO_4 + SO_3 + O.$$

The operation requires a standard permanganate, whose value is known upon a solution of ammonio-ferrous sulphate, containing about 30 gm. per litre. The method adopted by Le Blanc and Eckardt[1] is to dissolve about 2·5 gm. of the persulphate in water and dilute to 100 c.c. 10 c.c. of this solution are placed in a flask with 5 c.c. of dilute sulphuric acid of 1·16 sp. gr., and a considerable excess of ferrous solution, say 100 c.c., then about 100 c.c. of distilled water at a temperature of 70° to 80° C. are added, and a rapid titration made with permanganate. The reaction is the more rapid the greater the excess of iron solution, within reasonable limits.

The standard solutions are best verified upon a persulphate of known purity in order to ascertain the comparative composition of any given sample.

Another method consists in decomposing the persulphate by means of potassium iodide, and titrating the iodine separated with thiosulphate solution. 2 to 3 gm. of the sample are dissolved in 100 c.c. of water, and 10 c.c. of the solution are treated with an excess of potassium iodide (0·25 to 0·50 gm.), and heated for 10 minutes in a drying oven at 60° to 80° C. The iodine is then titrated with $^N/_{10}$ thiosulphate, starch being added towards the end of the titration. In this case the effects of the process are best established upon a persulphate of known purity.

B. Grutzner[2] has discovered that arsenious acid is completely oxidized to arsenic acid by alkali persulphates in alkaline solution.

In applying this reaction, about 0·3 gm. of the alkali persulphate is heated gradually to boiling with 50 c.c. of $^N/_{10}$ As_2O_3 and a few c.c. of potash or soda-lye, then digested for a short time, allowed to cool, the liquid made faintly acid with sulphuric acid, then strongly alkaline with sodium bicarbonate, and the excess of arsenious acid titrated back with $^N/_{10}$ iodine solution.

Marie and Bunel[3] from careful experiments advocate the following method for alkali persulphates :

Dissolve about 0·3 to 0·4 gm. of the sample in 100 c.c. of water; neutralize the solution, which is generally acid, in the presence of methyl orange; then add 2 c.c. of methylic alcohol, heat for 5 minutes to 70°-80°, and then boil for 10 minutes, cool, and titrate with methyl orange and decinormal soda.

---

[1] *C. N.*, **81**, 38.

[2] *Chem. Centr.*, 1900, 435.

[3] *Bull. Soc. Chim.*, **29**, *No.* 18

1 c.c. of decinormal soda corresponds to 0·0135 gm. $K_2S_2O_8$.
1 ,, ,, ,, ,, 0·0119 ,, $Na_2S_2O_8$.
1 ,, ,, ,, ,, 0·0114 ,, $Am_2S_2O_8$.

The use of methyl alcohol is based on the fact that a persulphate transforms a portion of the alcohol into aldehyde according to a well-known reaction. The method gave very satisfactory results.

TIN.

Sn = 118·7.

Metallic iron × 1·0628 = Tin.
Ferrous ammonium sulphate × 0·1513 = ,,
Factor for N/10 iodine or permanganate solution. 0·005935

THE method, originally devised by **Streng**, for the direct determination of tin by potassium dichromate, or other oxidizing agent in acid solution, has been found most unsatisfactory, from the fact that varying quantities of water or acid seriously interfere with the accuracy of the results. The cause is not fully understood, but that it is owing partly to the oxygen mechanically contained in the water reacting on the very sensitive stannous chloride there can be very little doubt, as the variations are considerably lessened by the use of water recently boiled and cooled in closed vessels. These difficulties are set aside by the processes of Lenssen, Löwenthal, Stromeyer, and others, now to be described, which are found fairly satisfactory.

1. Direct Titration by Iodine.

Lenssen's Method.—Add 1 or 2 gm. of Rochelle Salt. The cold solution is then titrated with N/10 iodine. The method has been almost entirely superseded by the titration with iodine in acid solution.

Titration of Stannous Chloride in Cold HCl Solution with Standard Iodine.[1] (**Pearce-Low Method.**)—This is one of the simplest, shortest, and most accurate for the volumetric determination of tin. It depends on the oxidation of $SnCl_2$ to stannic chloride by means of iodine in the presence of cold hydrochloric acid, thus:—

$$SnCl_2 + 2HCl + I_2 = SnCl_4 + 2HI.$$

Starch solution is used as indicator. A small amount of H_2SO_4 is not objectionable, but nitric acid and nitrates must not be present.

Solution Required.—The standard iodine solution generally used is made by dissolving 10·7 gm. of iodine in a solution of 20 gm. of potassium iodide in 50 c.c. of water, and making up with water to 1 litre.

When 0·5 gm. of sample is taken,

1 c.c. = 1 per cent. tin.

It may be standardized against tin or arsenious oxide.

Few of the metals ordinarily met with in materials to be analysed for tin interfere with this method, thus nickel, cobalt, aluminium, zinc, lead, etc., have no effect unless present in such large amounts that their colour masks that of the indicator.

---

[1] R. L. Hallett, *J. S. C. I.*, 1916, **35**, 1087.

METHOD OF PROCEDURE: Dissolve 0·5 to 2 gm. of the sample, according to percentage of tin present, in HCl, transfer the solution to a 350 c.c. wide-mouth conical flask, add HCl in quantity sufficient to bring up the free strong acid present to 50 c.c. and dilute the solution to 200 c.c. (The solution should contain 25 to 40 per cent. by volume of free strong HCl.) A coil of heavy sheet nickel (4 × 1½ inches), with narrow strip on one side, is then immersed in the solution, the strip being bent over the edge of the flask, and the latter is covered with a watch glass. The solution is heated to boiling and maintained in gentle ebullition for 30 minutes after all the iron, which may be present, is reduced, the change being indicated by the yellow liquid becoming pale green. It has been found that 30 minutes is always more than sufficient for the complete reduction of the stannic chloride from 0·5 gm. of tin oxide. The solution is cooled in an atmosphere of CO_2 generated by adding two ½-inch cubes of marble to the solution. The nickel coil is then removed, being washed with cold HCl (1 : 3) as it is withdrawn from the flask. Starch solution is then added and the solution titrated at once with standard iodine, the temperature of the liquid not being higher than 22° C.

In place of sheet nickel, reduction may be effected by the use of pure soft iron rods, sheet aluminium, or finely powdered antimony.

A tin determination may be made by this method in about 1½ hour, the results being accurate to about 0·1 per cent.

Note on the Effect of Interfering Metals.—Precipitation of metallic antimony by the nickel coil may be prevented by the addition of an extra 25 c.c. of HCl. Traces of copper do not influence the results, but if more than 0·05 gm. be present it should be removed beforehand by treatment with nitric acid, as in the case of titanium (see below). Bismuth is precipitated in metallic form in the reduction process, but the precipitate does not materially affect the titration. Tungsten is also precipitated as a blue oxide, which in small quantities is negligible in its effect, but, if necessary, may be filtered off and the solution again reduced before titration. Titanium is best removed by converting the tin into oxide by evaporation with nitric acid, fusing the residue for 5 minutes with acid potassium sulphate, dissolving the melt in dilute sulphuric acid, and filtering the solution. Any tungsten present may then be separated from the tin by treatment with ammonium carbonate solution, in which the tin is insoluble. Ferrous chloride is not oxidized during the titration, unless a large amount of iodine is added and allowed to stand for some time.

2. Indirect Titration by Ferric Chloride and Permanganate (Lowenthal, Stromeyer, etc.).

This method owes its value to the fact that when stannous chloride is brought into contact with ferric or cupric chloride it acts as a reducing agent, in the most exact manner, upon these compounds, stannic chloride being formed, together with a proportionate quantity of ferrous or cuprous salt, as the case may be. If either of the latter be then titrated with permanganate, the original quantity of tin may be found, the reaction being, in the case of iron—

$$SnCl_2 + Fe_2Cl_6 = SnCl_4 + 2FeCl_2.$$

55·84 iron = 59·35 tin. If decinormal permanganate, or the factor necessary to convert it to that strength, be used, the calculation by means of iron is not necessary.

METHOD OF PROCEDURE: The solution of stannous chloride, or other protosalt of tin in HCl, or the granulated metal, is mixed with pure ferric chloride (which, if tolerably concentrated, dissolves metallic tin readily, and without evolution of hydrogen) then diluted with distilled water, and titrated with permanganate as usual. To obtain the most exact results, it is necessary to make an experiment with the same permanganate upon a like quantity of water, to which ferric chloride is added, the quantity required to produce the same rose colour is deducted from the total permanganate, and the remainder calculated as tin.

Stannic salts, also tin compounds containing iron, are dissolved in water, HCl added, and a plate of clean zinc immersed for 10 or 12 hours; the tin so precipitated is carefully collected and washed, then dissolved in HCl, and titrated as above; or the finely divided metal may at once be mixed with an excess of ferric chloride, a little HCl added, and when solution is complete, titrated with permanganate. 4 eq. of iron (= 223·36) occurring in the form of ferrous chloride represent 1 eq. (= 118·7) of tin

or $$Fe \times 0{\cdot}53143 = Sn.$$

Tin may also be precipitated from slightly acid peroxide solution as sulphide by H_2S, the sulphide well washed, and mixed with ferric chloride, the mixture gently warmed, the sulphur filtered off, and the filtrate then titrated with permanganate as above. 4 eq. of iron = 1 eq. of tin.

Tin Ore.—In the case of analysis of cassiterite, Arnold[1] recommends that 1 gm. of the very finely powdered mineral be heated to low redness for 2 hours in a porcelain boat in a glass tube through which is passed a rapid current of dry and pure hydrogen gas, by which means the oxide is reduced to the metallic state. It is then dissolved in acid ferric chloride, and titrated with permanganate or dichromate in the usual way.

The Determination of Tin in White-metal Alloys.—Ibbotson and Brearley.[2] Tin may readily be determined by reducing the hot solution of the chloride, cooling in an atmosphere of CO_2, and titrating with iodine and starch. The reduction can be conveniently effected by means of iron, but any excess added must be dissolved completely. If antimony is present, it will be precipitated as metal, and cannot be dissolved again, but as cold acid solutions of stannic chloride are not reduced by antimony, which readily reduces them on heating, the solution may be directly titrated with iodine as usual, very good results being obtained. The antimony may be filtered off after the titration and determined, but the results obtained are rather low.

An improvement on the above method consists in reducing the stannic chloride with finely-powdered metallic antimony. The reduction of 0·15 gm. of tin is complete after boiling for 15 minutes, and the excess of antimony which remains undissolved acts as a safeguard during the cooling, since it reduces any tin which may have become oxidized whilst the solution is still hot. Cold solutions of stannous chloride take up oxygen less readily. The test analyses given show that the reduction is complete.

---

[1] *C. N.*, **36**, 238.

[2] *Ibid.*, **84**, 167.

The influence of various substances likely to be present in an ordinary analysis on the above method was examined, and it was found that the presence of iron, chromium, nickel, zinc, manganese, aluminium, bismuth, phosphorus, and sulphur is without effect on the results. The quantity of hydrochloric acid present should always be about one-fifth of the total volume. If copper is present, it will be reduced to the cuprous state, but accurate results may nevertheless be obtained if the iodine is added drop by drop to the vigorously agitated solution, so as to prevent the formation of a local excess of iodine. It is also advisable to have rather more hydrochloric acid present, up to about one-third of the total volume. Cobalt apparently gives very slightly higher values. Lead is without influence if sufficient hydrochloric acid is present to prevent the formation of lead iodide. The presence of arsenic completely vitiates the results, whether the tin is reduced with iron or with antimony. Mercury is reduced to the metallic state, but is not oxidized in cold solutions. If molybdenum or tungsten be present, a coloured lower oxide is formed, but this is not appreciably re-oxidized by the iodine, and the starch blue can be readily distinguished.

Colorimetric Method for the Determination of Tin in Food-Stuffs.—Dr. S. B. Schryver.[1] This method is based on the following reaction. When dinitrodiphenylamine-sulphoxide is treated with stannous chloride in the presence of hydrochloric acid in excess, it undergoes reduction as follows:—

$$C_{12}H_7(NO_2)_2NSO + 7SnCl_2 + 15HCl = C_{12}H_7(NH_2)_2NS, HCl + 5H_2O + 7SnCl_4.$$

The diaminothiophenylamine thus produced readily oxidizes, especially in the presence of minute quantities of ferric chloride, to a brilliant violet colouring matter (Lauth's violet), which forms the basis of the test.

Reagents Required: (*a*) 0·2 gm. of dinitrodiphenylamine sulphoxide is dissolved in 100 c.c. of $^{N}/_{10}$ NaOH and filtered. Of the reddish-brown solution so obtained 2 c.c. are used for each test. (*b*) Standard Tin Solution.—Stannous or stannic chloride (either may be used) containing 0·2856 gm. of tin in 100 c.c. Of this solution 5 c.c. are mixed with 5 c.c. of water, and 1 c.c. of this dilute solution contains 1·428 mgm. of tin, equivalent to 1 grain per lb. when 10 gm. of substance are used for the determination. (*c*) Strips of zinc foil, 2 inches by 0·5 inch, weighing about 0·75 gm. each.

PROCEDURE: 10 gm. of the food-stuff are introduced into a 700 c.c. round-bottomed Kjeldahl digestion flask, 10 gm. of potassium sulphate added, then 10 c.c. of concentrated sulphuric acid and the mixture heated over a small flame in one of the stands commonly used for that process. The heating is continued until the mixture has thoroughly charred and frothed up. It is often advisable to dilute the acid at first added and then gradually to concentrate. The effect of this dilution and subsequent concentration is to hydrolyse the proteins; the hydrolysis products are more readily oxidized by the sulphuric acid than the proteins themselves. An additional quantity of sulphuric acid is now added, and the heat gradually increased until the sulphuric acid can be rapidly boiled without danger of loss from frothing. 20 to 30 c c. are usually sufficient, but for meat extracts and jams as much as 40 c.c. of acid were found necessary. The heating is continued until all the organic matter has been destroyed and the contents of the flask are quite colourless, the whole process generally taking 2 to 3 hours. Food-stuffs containing but little water take longer. Care should be observed that sulphuric acid is present in sufficient quantity and that the contents of the digestion flask never become dry. After cooling, the contents of the flask are diluted to about 100 c.c., H_2S is passed in, and the mixture allowed to stand in a corked flask over night. Next day the flask is slightly warmed on a water-bath and the mixture of precipitated sulphide and sulphur filtered off through a small filter (4 cm). It should be noted that where a turbid solution is obtained in diluting the contents of the Kjeldahl flask (owing to separation of calcium sulphate) the precipitate should not be filtered off before passing in H_2S. The sulphide precipitate is washed a few times with water The filter paper containing the precipitate is next transferred to a test-tube and boiled with 5 c.c. of concentrated HCl to dissolve the sulphide. The solution is filtered through a small funnel into a wide-mouthed test-tube with side-tube connected with a pump. The filter paper is sucked as dry as possible and then washed with 2·5 c.c. of concentrated HCl. The test-tube is then closed by a cork carrying a tube reaching nearly to the surface of the liquid, through which a current of CO_2 is passed Whilst still hot, a piece of zinc (*c*) is thrown in to reduce the stannic chloride to stannous. When the last trace of zinc has dissolved, add the reagent (*a*) by a pipette, raising the cork for the purpose, but keeping the CO_2 passing the whole time. The solution is boiled for a minute or two, diluted to 100 c.c. with cold water, and filtered (using a pump). The liquid becomes violet during filtration and rapidly attains the full depth of colour after the addition of a drop of dilute ferric chloride solution.

---

[1] See *Local Government Board Report, No. 7.* On the presence of tin in certain canned oods. By Dr. Schryver. 1908.

Comparison is made against a set of standards containing 1, 0·75, 0·5, and 0·25 c c. of the dilute tin solution (*b*), these amounts being measured by a capillary pipette into 7·5 c.c. of concentrated HCl. A piece of zinc (*c*) is added, the stannic salt reduced to stannous in a current of CO_2, and the reagent (*a*) added, etc., as above.

The depth of colour is not strictly proportional to the amount of tin present. 0·25 grain per lb. gives a marked colour 1 grain per lb. gives a colour so deep that it is advisable to use less than 10 gm. for a determination or to use an aliquot part of the solution obtained after destruction of the organic matter. It is generally possible to determine immediately the degree of contamination by the depth of colour developed. Amounts of more than 1 grain per lb. should be determined gravimetrically, using 50 gm. of substance and weighing as SnO_2.

TITANIUM.

Ti = 48·1.

H. L. Wells and W. L. Mitchell[1] allude to a volumetric method of determining titanic acid by Pisani[2] which does not appear to have been found satisfactory. Marignac[3] applied Pisani's method to the determination of titanic acid in the presence of niobic acid, special conditions being adopted to avoid the reduction of the latter.

The authors have modified Pisani's process as improved by Marignac, and employ it for the determination of iron together with the titanic acid in ores. Sulphuric acid solutions are used, and the liquid is protected from the air during cooling and titration by means of a current of carbon dioxide.

Method of Procedure. 5 gm. of the pulverized ore are treated with 100 c.c. of concentrated hydrochloric acid in a covered beaker, using a gradually increasing heat, and adding more acid if necessary. When there is no further action, 50 c.c. of a mixture of equal volumes of sulphuric acid and water are added, and the liquid evaporated until it fumes strongly. After cooling, 200 c.c. of water are added, the whole heated until the sulphates dissolve, and the liquid filtered into a litre flask. If anything besides silicious matter is left on the filter-paper, it should be fused with potassium bisulphate, treated with concentrated sulphuric acid, and the sulphates dissolved in hot water and added to the main solution.

The liquid in the flask is made up to the mark with water, and four portions of 200 c.c. each taken, two in Erlenmeyer flasks (500 c.c.), and the other two in ordinary 350 c.c. flasks. Each of these represents 1 gm. of the ore.

To determine the iron, H_2S is passed into the solutions in the ordinary flasks to saturation, after which they are boiled until all the H_2S has been removed, care being taken to avoid any contact of the solution with the air by covering the mouths of the flasks with crucible lids. The flasks are then quickly filled to the neck with cold recently-boiled water, rapidly cooled, transferred to large beakers, and titrated with standard potassium permanganate.

To the solutions in the Erlenmeyer flasks 25 c.c. of concentrated sulphuric acid are added, and 3 or 4 rods of pure zinc, about 50 mm. long and 6 or 7 mm. in diameter are suspended in the liquid by means of a platinum wire attached to the loop of a porcelain crucible lid, which is inverted over the mouth of the flask. The liquid is then gently boiled for 30 or 40 minutes. Then, without interrupting the boiling, a rapid current of CO_2 is introduced under the cover. The flask is now rapidly cooled, the zinc washed with a jet of water and removed, and the solution titrated with permanganate, while the current of CO_2 is still being passed in. The difference between the permanganate used in this case and that required for the iron alone, represents the amount corresponding to the titanic acid. The factor for metallic iron divided by 0·7 gives the factor for titanic acid (TiO_2).

---

[1] *J. A. C. S*, 1895, **17**, 878.

[2] *Compt. Rend.*, 1864, **59**, 289,

[3] *Z. a. C.*, 1868, **7**, 112

The most convenient strength for the permanganate solution is one of 7·9 gm. per litre, corresponding to about 0·014 gm. of metallic iron.

In the determination of iron by reduction with sulphuretted hydrogen, no effect is produced on cold permanganate solution by the precipitated sulphur present, but precipitated sulphides, such as copper sulphide, should be filtered off before boiling.

The results of test analyses of recrystallized potassium titano-fluoride (K_2TiF_6) were somewhat low, but probably quite as good or better than any gravimetric method could furnish.

Another method for the determination of titanium and iron in iron, ores, etc., is given by Knecht and Hibbert,[4] as follows :—

METHOD OF PROCEDURE : About 0·5 to 1·0 gm. of the finely powdered ore is fused with about ten times its weight of caustic potash in a nickel dish. The melt, when cool, is treated with water, acidified with HCl, and the solution made up to 250 c.c. 25 or 50 c.c. are then transferred to a conical flask (of about 200 c.c. capacity) in which the titanic salt is reduced. The apparatus used is as shown in fig. 49. The flask is fitted with a rubber stopper having three holes. The central one carries a glass tube fitted with a Bunsen valve and through it passes a platinum wire carrying a zinc rod *r*. The other two holes are temporarily closed by glass rods. When the titanic solution has been transferred to the flask, HCl is added, and the flask closed by the stopper, and the zinc lowered into the liquid by means of the platinum wire passing through the small pierced rubber stopper, *c*. Reduction will be complete in 15 to 20 minutes, 20 minutes at least being necessary to ensure complete reduction when much iron is present. One of the glass rods, *a*, is then removed and a stream of carbon dioxide passed into the flask through a tube inserted in the same hole. The zinc is removed from the solution by raising the platinum wire, and the other rod *b* is then removed also. The zinc is washed with a little freshly-boiled water from a wash-bottle, the solution cooled, and titrated with *standard iron alum solution*, using potassium sulphocyanate as indicator. The *standard iron alum solution* consists of a solution of about **14** gm. iron alum dissolved in water, acidified with sulphuric acid till the liquid assumes a pale straw colour, and made up to 1 litre. By measuring the exact volume of standard titanous chloride solution (see p. 240) required to reduce 25 c.c. of this iron-alum solution, using potassium sulpho-cyanate as indicator, its strength is determined, and as it will retain the same strength for an indefinite period, this iron alum solution may be used in all subsequent cases for standardizing the titanous chloride solution.

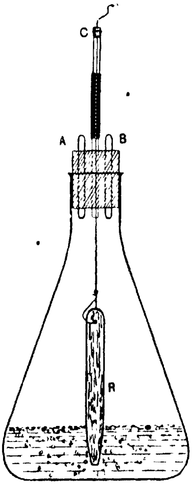

FIG. 49.

---

[4] *New Reduction Methods in Volumetric Analysis*, by Knecht and Hibbert, 1910.

Ex. 0·4997 gm. of rutile treated as above and made up to 250 c.c.

25 c.c. after reduction with zinc and hydrochloric acid, required 17·3 c.c. of iron alum solution.

1 c.c. of iron alum solution contained

$$0·001842 \text{ gm. Fe} = \frac{·001842 \times 80·1}{55·85} = 0·002642 \text{ gm. } TiO_2.$$

$$\text{Hence } \frac{·002642 \times 17·3 \times 100}{0·04997} = 91·46 \text{ per cent. } TiO_2.$$

Also, 1·960 gm. treated in the same way, and titrated with titanous chloride, required 26·1 c.c.

$$1 \text{ c.c. } TiCl_3 = 0·001432 \text{ gm. Fe} = 0·002047 \text{ gm. } Fe_2O_3.$$

$$\text{Hence } \frac{0·002047 \times 26·1 \times 100}{1·96} = 2·73 \text{ per cent. } Fe_2O_3.$$

A. Gemmell's[1] method is a modification of Newton's[2] (reduction by means of zinc and sulphuric acid, introducing an excess of ferric sulphate, and titrating the ferrous salt produced with permanganate).

METHOD OF PROCEDURE: A zinc-aluminium alloy (Zn 90 per cent., Al 10 per cent.) is used as the reducing agent, the reduction being conducted at about 50° C. in a flask fitted with a rubber stopper and Bunsen valve. The reduced solution is cooled, filtered under diminished pressure into a flask containing ferric sulphate and dilute sulphuric acid, the air having been previously swept out by the addition of solid sodium carbonate, and the contents of the flask titrated with standard permanganate. The time required for the reduction of quantities up to 0·05 gm of titanium dioxide at 50° C. is from 5 to 8 minutes. With larger amounts a much longer time is necessary, and it is advisable to allow a stream of carbon dioxide to play over the funnel during the filtration. For amounts of TiO_2 above 0·15 gm. the method is inaccurate, owing to incomplete reduction and oxidation during filtration.

With titaniferous rocks and minerals, the total iron and titanium oxides are determined together in one portion, and the ferric oxide alone in another portion. For the total oxides the time required for reduction is usually 30 to 45 minutes. The reduction of ferric iron alone is complete in 3 to 6 minutes, the end-point being found by testing with thiocyanate. All the iron will be reduced before the titanium. The solution is cooled, filtered, and titrated with permanganate. No special precautions are taken to prevent oxidation during filtration, as any reduced titanium is re-oxidized. 1 c.c. $^{N}/_{10}$ permanganate = 0·008 gm. TiO_2.

URANIUM.

U = 238·2.

THE determination of uranium may be conducted with great accuracy by permanganate, in precisely the same way as ferrous salts (p. 237). The metal must be in solution either as acetate, sulphate, or chloride, but not as nitrate. In the latter case it is necessary to evaporate to dryness with excess of sulphuric or hydrochloric acid, or to precipitate with alkali, wash and redissolve in acetic acid.

---

[1] *Analyst*, 1910, **35**, 198. [2] *Amer. Jour. Science*, 1908, **25**, 130.

The reduction to the uranous state is made with zinc, but as the end of reduction cannot, like iron, be known by the colour, it is necessary to continue the action for a certain time; in the case of small quantities for a quarter, of larger for half an hour, at a temperature of 50° to 60° C., and in the presence of excess of sulphuric acid; all the zinc must be dissolved before titration. The solution is then freely diluted with boiled water, sulphuric acid added if necessary, and then permanganate until a faint permanent rose colour is obtained. The ending is distinct if the solution be well diluted, and the reaction is precisely the same as in the case of ferrous salts, namely, 2 eq. of uranium existing in the uranous state require 1 eq. of oxygen to convert them to the uranic state; hence 55·84 Fe = 119·1 U, or 1 of iron = 2·133 of uranium, consequently the strength of any permanganate solution in relation to iron being known, it is easy to find the amount of uranium.

Since uranyl solutions are not reduced by sulphurous acid, in a mixture of ferric sulphate and uranyl sulphate first the iron can be reduced with sulphurous acid and titrated with permanganate, then the uranyl salt in this titrated solution reduced by zinc and titrated as described above.

Another method of determining uranium has been published by B. Glasmann.[1]

The method depends on the reaction of neutral solutions of uranyl salts on a mixture of potassium iodide and iodate—

$$3UO_2(NO_3)_2 + 5KI + KIO_3 + 3H_2O = 3UO_2(OH)_2 + 6KNO_3 + 3I_2.$$

Any excess of acid in the solution must be neutralized with sodium carbonate, which is added till a precipitate begins to be permanent; this precipitate is then just redissolved in dilute acid. Place the solution in a 300 c.c. distillation flask provided with a ground stopper carrying a funnel with stop-cock, the tube of which reaches to the bottom of the flask. Insert the exit tube of the flask into the receiver containing potassium iodide solution, add to the uranyl solution the requisite amount of iodide and iodate mixture, dilute to 120 c.c., close with the stoppered funnel, and slowly heat to boiling. When boiling, cool the receiver with water, and lead a stream of hydrogen through the boiling liquid. When the liquid is reduced to 50 c.c., withdraw the flask from the receiver, remove the burner, wash the delivery tube into a beaker, rinse the contents of the receiver into the same beaker, and titrate with thiosulphate. With 0·2 to 0·3 gm. of uranyl compound the whole operation requires 20 minutes. The results are accurate, and are not affected by the presence of alkaline-earth chlorides.

VANADIUM.

V = 51.

VANADIUM salts, or the oxides of this element, may be very satisfactorily titrated by reduction with a standard ferrous solution: thus—

$$2FeO + V_2O_5 = Fe_2O_3 + V_2O_4.$$

---

[1] *Ber.*, 1904, **37**, 189.

1 gm. of Fe represents 1·630 gm. of vanadic pentoxide.

Of course it is necessary that the vanadium compound should be in the highest state of oxidation, preferably in pure sulphuric acid solution. The blue colour of the tetroxide in the dilute liquid has no misleading effect in testing with ferricyanide.

With hydrochloric acid great care must be taken to ensure absence of free Cl or other impurities. The end-point in the case of this acid is different from that with sulphuric acid, owing to the colour of the ferric chloride, the mixture becoming clear green.

The accuracy of the action is not interfered with by ferric or chromic salts, alumina, fixed alkalis, or salts of ammonia.

Vanadic solutions being exceedingly sensitive to the action of reducing agents, great care must be exercised to exclude dust or other carbonaceous matters, alcohol, etc.

The reduction of vanadic acid by hydriodic or hydrobromic acid; and its titration in alkaline solution with iodine has been worked out by P. E. Browning.[1] The solution containing the vanadate is boiled in a conical beaker with potassium iodide or bromide, in not too large a quantity, and a regulated amount of sulphuric acid, until no more iodine or bromine is liberated. After cooling, the residual liquid is nearly neutralized with aqueous potash, a small quantity of tartaric acid is added, and the solution made alkaline by addition of potassium bicarbonate. Excess of standard iodine is then added, and after remaining for half an hour in a well-closed bottle, the free iodine left is determined by means of a solution of arsenious oxide in the usual way.

One mol. of iodine represents 1 mol. of vanadium pentoxide, or

$$\text{iodine} \times 0·717 = V_2O_5.$$

Determination of Vanadium (and Chromium) in Steel.—The following method[2] is given by J. Kent Smith, American Vanadium Co., Pittsburg, Pa., U.S.A.

Dissolve 4 gm. of the steel in 48 c.c. of water and 12 c.c. of strong sulphuric acid, and when dissolved oxidize with nitric acid, avoiding a great excess. Evaporate to dryness on a hot plate, take up with 150 c.c. of water and boil till dissolved. Add 10 c.c. (or excess) of a $2\frac{1}{2}$ per cent. permanganate solution, and boil for 5 minutes; then add a little manganese sulphate to precipitate any undecomposed permanganate. Cool, dilute to 500 c.c., filter through a dry filter and take 375 c.c. (= 3 gm. Steel) of the clear filtrate. To this latter add 50 c.c. of dilute sulphuric acid, then a measured excess of $^{N}/_{10}$ ferrous sulphate and titrate back with $^{N}/_{10}$ permanganate till permanently pink: each c.c. of permanganate thus used up equals 0·001743 gm. chromium. Now add 1 or 2 c.c. of ferrous sulphate solution to dissolve any MnO_2 that may have been formed, and add permanganate *very gradually* until the solution is just pink, then cautiously add $^{N}/_{20}$ ferrous sulphate until the pink is just discharged (this should be done exactly to one drop). Next add a carefully measured 5 c.c. (or excess) of $^{N}/_{20}$ ferrous sulphate, and titrate back with $^{N}/_{20}$ dichromate, using potassium ferricyanide as indicator. 1 c.c. $^{N}/_{20}$ dichromate = 0·00255 gm. Vanadium.

---

[1] *J. Amer. Sci.*, 1896, 185.

[2] See Macfarlane's *Laboratory Notes on Iron and Steel Analyses*, p. 222 (1909).

In place of $^{N}/_{10}$ ferrous sulphate decinormal solution of ferrous ammonium sulphate, containing 39·214 gm. of the pure crystals to the litre, may be used. As an average standardization 1 c.c. = 0·001718 gm. Cr.

In the vanadium titration a 5 per cent. solution of potassium ferricyanide is used as indicator.

Method of Procedure in the Absence of Chromium. Dissolve 2·5 gm. of a vanadium steel in 30 c.c. of sulphuric acid (1 : 3), adding 10 c.c. of nitric acid when solution is near completion. Evaporate till fumes are evolved. Add 100 c.c. sulphuric acid (1 : 3), then water to about 400 c.c. Heat to 60° or 70° C. and add dilute permanganate solution drop by drop until a faint pink colour persists. Discharge this colour exactly by careful addition of ferrous sulphate solution. Add 50 c.c. of 10 per cent. sodium phosphate solution, and cool. Add an excess of standard ferrous sulphate, and titrate back with dichromate, using potassium ferricyanide as indicator.

1 c.c. $^{N}/_{10}$ ferrous sulphate = 0·0051 gm. V.

ZINC.

Zn = 65·37.

1 c.c. $^{N}/_{10}$ solution = 0·003268 gm. Zinc.
Metallic iron × 0·5852 = Zinc.
" × 0·7285 = Zinc oxide.
Ferrous ammonium sulphate × 0·0836 Zinc.
" " " × 0·1041 = Zinc oxide.

1. Precipitation as Sulphide with Ferric Indicator (Schaffner).

Iron, copper, lead, cadmium, manganese, nickel and cobalt interfere and must previously be removed—the two latter hardly ever occur in appreciable quantities in ores of zinc.

Standard Solution Required.—Sodium sulphide, prepared from a cold saturated solution of crystallized sodium sulphide by dilution with 10 to 20 times its volume of water.

Method of Procedure: Of the finely powdered sample, previously dried at about 105°, 0·5 gm. (or 1 to 2 gm. in the case of poor ores) is placed in a beaker, aqua regia added, and evaporated nearly to dryness on a hot plate. The residue is taken up with hot water, 20 c.c. of ammonia and 10 c.c. of ammonium carbonate solution (10 per cent.) added, then, if necessary, a few drops of a solution of permanganate to precipitate lead and manganese. Heat nearly to boiling and filter into a 500 c.c. flask, wash the precipitate well with hot water containing ammonia until a drop of the washings shows no reaction with sodium sulphide. The filtrate and washings, which should measure about 250 c.c., are heated to about 50°, a drop of a solution of ferric chloride added, and the standard sodium sulphide solution run in gradually from a burette with constant shaking till the flakes of ferric hydrate become converted into black FeS. The titration is then complete.

The standardization of the sodium sulphide solution is carried out similarly. 0·5 gm. of pure zinc is dissolved in 10 c.c. of HCl in a flask, hot water added, then 20 c.c. of ammonia and 10 c.c. of ammonium carbonate followed by a drop of ferric chloride as above, and the solution diluted to about 250 c.c. The sodium sulphide solution is then added rapidly at first and 0·1 c.c. at a time towards the end.

A convenient strength is 70 c.c. of sulphide = 0·5 gm. Zn.

A simple calculation gives the percentage of zinc in the sample.

For greater accuracy measure the solution at completion of the titration and deduct 0·6 c.c. from the burette reading for every 100 c.c. of the solution, applying this correction to the standard also. This allowance is based on the observation that 0·6 c.c. of a sulphide solution of the above strength is required to blacken 100 c.c. of dilute ammonia to which a drop of ferric chloride has been added.

Copper, etc., when present, must first be separated by the ordinary well-known methods.

Determination of Zinc in Blende by the Modified Schaffner Method.

According to a communication from v. Hassreidter and E. Prost,[1] the above method is now employed at zinc works.

Preparation of the Solution.—2·5 gm. of the blende, which has been dried at 100° and finely ground, are treated with 12 c.c. of fuming nitric acid in a 200 c.c conical flask, first in the cold, then with gentle heating till all red fumes have been dissipated, when 20 to 25 c.c. of strong nitric acid are added and the whole evaporated to dryness on the sand-bath. 5 c.c. of hydrochloric acid and a little water are then added and the mixture warmed until as much as possible has dissolved. 50 to 60 c.c. of water are then added and the whole heated to 60° to 70°, until only gangue and separated sulphur remain undissolved.

A moderate current of H_2S is next passed into the solution and 50 to 100 c.c. of cold water added, little by little, with continuous stirring until the precipitation of lead and cadmium sulphides is complete, which may be judged by the transparency of the bubbles as they rise through the solution.

Excessive dilution and too slow a current of H_2S should be avoided. The liquid is filtered and the precipitate washed with 100 c.c. of H_2S water, to which 5 c.c. of HCl have been added, until a drop of the filtrate ceases to give the reaction for zinc with ammonium sulphide. The filtrate and washings (about 300 c.c. together) are boiled till H_2S is entirely removed, as shown by lead acetate paper, and ferrous iron then oxidized, by addition of 5 c.c. of strong nitric acid and 10 c.c. of HCl.

After partial cooling the solution is transferred to a 500 c.c. measuring flask, 100 c.c. of ammonia (sp. gr. 0·9 to 0·91) and 10 c.c. of a cold saturated solution of commercial ammonium carbonate added, and the whole well shaken and allowed to cool (in the presence of manganese 10 c.c. of hydrogen peroxide are added before the ammonia).

In the meantime an ammoniacal zinc solution of known content is prepared by dissolving in a 500 c.c. measuring flask chemically pure zinc, approximately equal in quantity to the zinc content of the ore, in 5 c.c. of nitric acid and 20 c.c. of HCl diluted with about 250 c.c. of water. After solution, 100 c.c. of ammonia and 10 c.c. of ammonium carbonate solution, as above, are added, the whole shaken and allowed to cool. When quite cold, both flasks are filled to the mark with water and the solution prepared from the ore passed through a dry folded filter.

---

[1] Given in Lunge's *Tech. Methods of Chem. Analysis*, Vol. I., Part 1, p. 289, *et seq.*

Standard Solution of Sodium Sulphide. A concentrated solution of commercial sodium sulphide crystals is diluted with 10 to 20 times its volume of water, so that

$$1 \text{ c.c.} = 0{\cdot}005 \text{ to } 0{\cdot}010 \text{ gm. zinc.}$$

($Na_2S, 9H_2O$ is soluble in twice its weight of water. 3·67 gm. of the crystals correspond to 1 gm. of zinc.)

Method of Titration.—For titration 100 c.c. are pipetted from each 500 c.c. flask as above into thick-walled glass cylinders or beakers and about 200 c.c. of water added to each. Two 50 c.c. burettes are then filled with standard sodium sulphide solution, which is run from each alternately into the solutions in the beakers, at first in 2 or 3 c.c. at a time and later in such smaller quantities as may appear necessary.

The solutions are stirred and a drop of each placed simultaneously, by means of thin glass rods, on a strip of sensitive lead acetate paper. After 10 to 15 seconds the drops are washed off by the aid of a small wash-bottle, and the titration continued until the drops taken from the two solutions, after an equal lapse of time, give weak but distinctly perceptible brown stains of equal intensity.

Should the volume of liquid withdrawn for the tests be appreciable, the operation must be repeated; in all cases the end-reactions in the two solutions must be reached at the same time and the readings made to 0·05 c.c. (1 drop usually).

Let a gm. of zinc be dissolved to make 500 c.c. of standard solution for comparison, and
b = number of c.c. of sodium sulphide solution required per 100 c.c. of the above,

then 1 c.c. of sodium sulphide $= \frac{a}{5b}$ gm. zinc and if n c.c. of this are required per 100 c.c. of the solution of the ore (= 0·5 gm.), then the percentage of zinc in the latter $= 200\,n \times \frac{a}{5b} = \frac{40na}{b}$.

In very exact determinations a quantity of ferric chloride corresponding to the iron content of the ore, should be added to the standard solution to compensate for the zinc carried down with the ferric hydroxide precipitate.

2. Determination as Ferrocyanide in Hydrochloric Acid Solution (C. Fahlberg).

This method is not available in the presence of lead, copper, cadmium, iron, manganese, nickel or cobalt.

Preparation of the Zinc Solution.—(1) *Zinc in the presence of iron* *and no more than a small percentage of lead.* 5 or 10 gm. of the substance are dissolved in hot dilute HCl in a covered beaker, and when action has ceased, the liquid is filtered into a 500 c.c. measuring flask, the residue well washed with hot water, and the flask cooled and made up to the mark with water.

50 c.c. (= 0·5 or 1 gm. of substance) are then pipetted into a beaker, the liquid heated, bromine water, hydrogen peroxide, or sodium hypochlorite (but not nitric acid) added to oxidize the iron, then 0·96 ammonia in excess. The ferric hydroxide is filtered off, washed with hot water and a little ammonia, and if large in amount, is redissolved in HCl and reprecipitated, the filtrate and washings being added to the main bulk. This is then concentrated to about 200 c.c., neutralized with HCl and 10 c.c. more added. The hot solution is then ready for immediate titration.

(2) *Zinc in the presence of iron and manganese.* Von Schulz and Low's method,[1] as modified by Pattinson and Redpath[2] should be used as follows (applicable to blende, flue-dust, etc.):

Treat 1 gm. of the finely powdered ore in a covered beaker with HCl, heat gently, and after some time add HNO_3. Evaporate to dryness, and extract the residue with 1 gm. of ammonium chloride and 3 to 5 c.c. of ammonia; redissolve the residue in hydrochloric acid, evaporate to dryness, and extract a second time, using the same quantities of ammonium chloride and ammonia as before. Filter, and wash several times with hot chloride of ammonium solution of 5 per cent. strength. If manganese is present, precipitate it by adding bromine-water to the ammoniacal solution, filter, redissolve the precipitate in hydrochloric acid, add ammonium acetate, precipitate by H_2S any zinc carried down with the manganese, dissolve the ZnS in hydrochloric acid, and add it to the main solution. Add hydrochloric acid till the solution is just acid, then a further 10 c.c. and titrate the solution hot, reserving a portion at first in case too much ferrocyanide should be run in. Use uranium acetate spotted on a white porcelain plate as indicator. (*When copper is present*, it is removed by Seaman's method, see below.)

W. H. Seaman[3] recommends the use of aluminium (in place of granulated lead previously recommended, which gave rise to high results) for the removal of copper, the process being carried out as follows:

0·5 gm. of the ore is covered with 7 c.c. of concentrated nitric acid, and an equal volume of hydrochloric acid is then added. The mixture is allowed to act for 15 minutes at a temperature not exceeding 60° C. 7 grams of ammonium chloride are now introduced, and the whole evaporated to dryness. After making alkaline with 5 c.c. of ammonia, 15 c.c. of bromine water are added, and the mixture is boiled for minutes, filtered hot, and the precipitate washed with a mixture of ammonium chloride and ammonia. The filtrate faintly acidified with hydrochloric acid, is boiled for 3 minutes with aluminium foil, which precipitates all the copper, lead and cadmium. The foil is then removed, and the liquid titrated hot, the precipitated metals in no way interfering.

---

[1] *J. S. C. I.*, 1892, **11**, 846.

[2] *Ibid*, 1905, **24**, 228.

[3] *J. A. C. S.*, 1907, **29**, 205-211 and *J. S. C. I.*, 1907, **26**, 258.

Effect of Lead.—Lenher and Meloche[1] find that lead does not interfere with this determination when carried out as described above, viz., in presence of HCl and ammonium chloride. They recommend 10 c.c. concentrated HCl and 10 gm. of ammonium chloride in 200 c.c. as convenient quantities to have present. Concentrations of the latter as high as 20 per cent. give rise to an indistinct end-point, but sharp end points are obtained with a range of 1·5 to 6 per cent. of free HCl. As indicator they recommend a 5 per cent. solution of uranium nitrate. Beringer in an experiment in which 20 c.c. of a zinc solution required 20·3 c.c. of standard ferrocyanide found that when another 20 c.c. of the same solution, to which 0·05 gm. of lead (as chloride) had been added, was titrated 20·9 c.c. of ferrocyanide were required.

The Process.—Solutions required :

(*a*) Standard potassium ferrocyanide. Dissolve 43·2 gm. of the pure crystals ($K_4 FeCy_6, 3H_2O$) in water, filter into a litre flask and make up to the mark.

1 c.c. = 0·01 gm. zinc.

(*b*) A strong solution of uranium acetate or nitrate (as indicator).[2]

The zinc solution, obtained as described above, should be approximately 200 c.c. in volume, and, if more, evaporated to that volume before the final 10 c.c. of HCl are added. About nine-tenths of the hot solution (60° to 80°) are then emptied into a basin and standard ferrocyanide run in, a few c.c. at a time, bringing a drop of the well-stirred solution after each addition into contact with a drop of the indicator on a white porcelain plate. When a brown tinge is thus shown, the reserved portion of zinc solution is transferred to the basin and the addition of ferrocyanide continued cautiously till a drop just gives a light brown colour with a drop of the uranium solution. Should an excess of ferrocyanide be added, which would, of course, spoil the test, 1 c.c. of a solution of zinc chloride containing 10 gm. of pure zinc in 1 litre should be added by means of a capillary pipette (a drop of the solution being titrated should now cease to give a brown tinge with a drop of the indicator, otherwise another c.c. of zinc chloride must be added), and the titration finished as above making allowance for the amount of zinc thus added, if any.

The standard ferrocyanide solution is standardized as follows : 0·4 gm. of pure zinc (or 0·5 gm. of pure zinc oxide, which contains 0·4017 gm. zinc) is dissolved in HCl and water, 5 gm. of pure ammonium chloride added, the solution made just ammoniacal, then just acid by addition of HCl, finally 10 c.c. more HCl are added. The hot solution, made up to 200 c.c. approximately, is then titrated. If not of exact strength, the correct value should be marked on the bottle. The solution keeps well, but should be restandardized from time to time.

A modification of the ferrocyanide method so as to be available for the determination of both **zinc and manganese** in the presence of each other has been devised by G. C. Stone.[3]

---

[1] *Analyst*, 1912, **37**, 585.

[2] Greenwood and Brislee state that ammonium tetramolybdate is nearly twice as delicate an indicator as the uranium salt, and recommend its use. See *J. S. C. I.*, 1909, **28**, 1138.

[3] *J. A. C. S.*, 1895, **17**, 437.

The standard solutions required are:—

Potassium ferrocyanide, about 30 gm. per litre. Its actual working strength is found by titrating it upon a known weight of either zinc or manganese in slightly acid solution, using a very dilute solution of cobalt nitrate as outside indicator. A correction is made in all cases for the amount of ferrocyanide required to give the reaction with the indicator, and may be taken as 0·5 c.c. for every 100 c.c. of the solution titrated.

Potassium permanganate, 1·99 gm. of the pure salt per litre. 1 c.c. = 1 mgm. of Mn.

The end-point of reaction with the indicator is found by placing drops of the cobalt solution on a white tile, and bringing a drop of the liquid under titration in contact with it, but not actually mixing. The immediate production of a faint green line at the junction of the drops is accepted as the correct reading.

METHOD OF PROCEDURE: The ore is dissolved in HCl with the addition of $KClO_3$ as an oxidizer, and care must be taken to have sufficient acid to keep all the manganese in solution.

Lead alone need not be separated; copper can be precipitated by lead; or lead and copper can both be precipitated by aluminium. Cadmium should be precipitated by H_2S, and the filtrate oxidized. Iron and aluminium are best separated by barium carbonate, but the latter must be free from alkali carbonates and hydroxides, barium hydroxide, and ammonium salts. A salt sufficiently pure for the purpose may be obtained by suspending the ordinary pure carbonate (first proved free from ammonium salts) in warm water for several hours with 2 or 3 per cent. of its weight of barium chloride.

The well-oxidized solution of the ore is put into a 500 c.c. flask, and barium carbonate suspended in water added until the precipitate coagulates. The whole is then poured into a beaker, well mixed, allowed to settle, and the clear liquid decanted through a dry filter, and diluted to 500 c.c. Portions of 50, 100, or 200 c.c. of the filtrate are used for each titration. One portion, which should contain between 0·01 and 0·04 gm. of manganese, is diluted to 200 c.c., heated nearly to boiling in a porcelain dish, and titrated rapidly with permanganate with vigorous stirring.

A second portion is made slightly acid with hydrochloric acid, the zinc and manganese are titrated together in the cold with ferrocyanide; the dark colour of the precipitate suddenly changes to light yellowish green shortly before the end of the reaction. It is not necessary to test with the cobalt solution until 1 or 2 c.c. of the ferrocyanide have been added after the lightening of the precipitate.

EXAMPLE: 1 c.c. of the ferrocyanide solution equalled 0·00606 gm of zinc, or 0·00384 of manganese; 1 c.c. of the permanganate equalled 0·001 gm. of manganese. 2½ gm. of the ore were dissolved, and the iron precipitated and filtered off. 50 c.c. of the solution were diluted, heated, and titrated with permanganate, requiring 18·45 c.c. = 7·38 per cent. of manganese. 100 c.c. titrated with ferrocyanide required 27·85 c.c. of which 9·61 c.c. would be used by the manganese present. Deducting this, 18·24 c.c. was left for the zinc, equal to 0·11053 gm., or 22·11 per cent. The amounts of zinc and manganese as determined gravimetrically were 22·05 and 7·58 per cent. respectively.

3. Determination as Zinc-Ammonium Phosphate.

The method has been devised by P. H. Walker.[1] According to Greenwood and Brislee[2] it is of limited application only, the results being seriously affected in the presence of lime and magnesia. This process is a modification of that devised by Stolba for the determination of magnesium, and is carried out as follows:—

To the zinc solution, which should contain ammonium chloride, a large excess of ammonia is added, then a large excess of sodium phosphate solution. Hydrochloric acid is now gradually added until, after stirring, the solution remains milky, when the liquid is heated to about 75° C., and the gradual addition of acid continued, with constant stirring, until nearly complete neutralization is attained. By this means the precipitate becomes crystalline, and after 5 minutes' standing it should be filtered off and washed with cold water until the washings show only a faint trace of chloride. The filter paper and precipitate are now returned to the beaker in which the precipitation was carried out, an excess of standard acid added, and the exact point of neutrality determined by means of standard alkali, using methyl orange as indicator. From the equation—

$$ZnNH_4PO_4 + H_2SO_4 = ZnSO_4 + NH_4H_2PO_4$$

it is seen that 1 c.c. of normal acid corresponds with 32·7 mgm. of zinc. Since the zinc ammonium phosphate is not precipitated in presence of a large excess of ammonia, any magnesium present, which will be precipitated, may be removed by filtration, and the filtrate neutralized to throw down the zinc. Fairly good results are obtained by this method also in the presence of iron, but any manganese must be previously separated, best by means of nitric acid and potassium chlorate.

J. M. Findlay and A. C. Cumming[3] have found that the results obtained by this method are inaccurate: (i) if the solution contained more than a trace of acetic acid, (ii) if the solution after the precipitation was alkaline, or (iii) if the solution contained sodium or potassium salts.

4. As Zinc Mercury Thiocyanate (Jamieson).[4]

Instead of weighing the precipitate of zinc mercury thiocyanate produced in Lundell and Bee's gravimetric method[5] for determining zinc in alloys, the precipitate is titrated with potassium iodate in the presence of strong hydrochloric acid and an immiscible solvent. The equation is

$$ZnHg(SCN)_4 + 6KIO_3 + 12HCl = ZnSO_4 + HgSO_4 + 2H_2SO_4 + 4HCN + 6ICl + 6KCl + 2H_2O.$$

The reagent used for the precipitation contains 39 gm. potassium (or ammonium) thiocyanate and 27 gm. mercuric chloride per litre, 25 c.c. of the reagent being used for 100 c.c. of zinc solution, the free acid in which should not exceed 5 per cent. Cadmium, cobalt, copper, bismuth, manganese, and mercurous compounds should be absent. Nickel in small amounts does not interfere appreciably. Ferric compounds in appreciable amounts should be reduced by SO_2. Arsenious compounds need not be removed.

---

[1] *J. A. C. S.*, 1901, **23**, 468.

[2] *J. S. C. I.*, 1909, **28**, 1138.

[3] *J. C. S.*, 1913, **29**, 153.

[4] *J. A. C. S.*, 1918, **40**, 1036.

[5] *J. S. C. I.*, 1914, **33**, 967.

METHOD OF PROCEDURE: The zinc mercury thiocyanate corresponding with 0·03 to 0·10 gm. of zinc is precipitated, collected on a washed filter with gentle suction, and washed four or five times with a solution containing 10 c.c. of the reagent in 500 c.c. The precipitate with the filter is transferred to an 8-ounce titration bottle, a thoroughly-cooled mixture of 35 c.c. strong hydrochloric acid and 10 c.c. of water, followed by 7 to 8 c.c. of chloroform, is added, and the liquid at once titrated rapidly with standard potassium iodate solution, while the bottle is well shaken. When the iodine liberated in the first stage of the reaction has disappeared, the stopper is inserted and the titration continued slowly, with thorough shaking after each addition, until the iodine colour has disappeared from the chloroform solution. This marks the end-point. If more than 50 c.c. of the iodate solution are required, a further 10 to 15 c.c. of strong hydrochloric acid must be added to prevent hydrolysis of the iodine monochloride.

Standard Iodate Solution.—19·644 gm. KIO_3 per litre.

1 c.c. = 0·001 gm. Zn.

Conversely, the method determines Mercury (q.v. p. 278).

5. Zinc and Lead.

Rupp[1] has devised the following method for the determination of zinc (and lead). It depends on the fact that when a neutral solution of zinc is added to a solution of potassium cyanide the soluble double cyanide $K_2Zn(CN)_4$ is formed at first, but the least excess of zinc causes the production of insoluble zinc cyanide. The method is inapplicable in the presence of acetates.

METHOD OF PROCEDURE: The solution of zinc as sulphate or chloride is neutralized by means of caustic soda, using methyl orange as indicator, and made up to a known volume. Into a flask containing about 0·5 gm. of ammonium chloride dissolved in a little water 20 c.c. of $^N/_2$ KCN is accurately measured, and the neutral solution of zinc is run in from a burette into this mixture, with constant agitation, until a permanent turbidity appears. The cyanide solution is standardized in the same way with a solution of pure zinc sulphate. The presence of a salt of ammonia is essential, as it causes the re-solution of precipitate locally formed in the cyanide solution. Too much ammonium chloride causes high results.

1 c.c. $^N/_2$ KCN = 0·008171 gm. Zn.

Lead.—Lead cyanide is not soluble in excess of alkali cyanide, but is readily so in acids. On adding excess of KCN to a lead solution and filtering, the excess of KCN can be titrated with HCl. The solution of lead as nitrate is neutralized by means of NaOH, using methyl orange as indicator, and added to 25 c.c. of $^N/_2$ KCN solution contained in a 100 c.c. measuring flask, the amount of lead present being such that an excess of cyanide remains after it has all been precipitated as $Pb(CN)_2$. The flask is made up to the mark, well shaken, allowed to stand for 10 minutes, and filtered. 50 or 75 c.c. of the filtrate are then titrated with $^N/_2$ or $^N/_4$ HCl, using methyl orange as indicator.

---

[1] *Chem. Zeit.*, 1910, **34**, 121.

$$1 \text{ c.c. } ^N/_2 \text{ HCl} = 1 \text{ c.c. } ^N/_2 \text{ KCN} = 0{\cdot}0518 \text{ gm. Pb.}$$
$$1\text{Pb} = 2\text{KCN} = 2\text{HCl}.$$

The cyanide is standardized by a pure lead salt.

6. Zinc Dust.

Zinc dust consists of an intimate mixture of finely divided metallic zinc (up to over 90 per cent.) and zinc oxide, together with some cadmium, iron, lead, arsenic, small particles of ground ore, and carbon. In commerce a product containing a guaranteed content of 90 per cent. of metal is usually demanded. The real content of metallic zinc can only be arrived at by a complete analysis.

The volume of hydrogen yielded by it on treatment with acids appears to be the most accurate, as suggested by Fresenius or by Barnes.[1] This may very well be done in the nitrometer with decomposing flask, comparing the volume of gas yielded by pure zinc and the sample of dust under examination.

L. de Koninck[2] has shown that it is necessary to avoid india-rubber connections in the apparatus used, as otherwise there is a loss of hydrogen, due to diffusion.

Many other methods have been proposed for the valuation of this substance. The best is that of Klemp,[3] which is as follows:—

Solutions Required: (*a*) *Potassium Iodate* solution, containing 15·25 gm. per 300 c.c.

(*b*) *Potassium Hydroxide*.—420 gm. per litre, or sodium hydroxide 300 gm. per litre.

The Process.—0·5 to 1 gm. of the well-mixed zinc dust is weighed in a tube, and poured into a 200 c.c. stoppered flask, the tube being again weighed. For every 0·1 gm. of zinc present 10 c.c. of the caustic alkali solution (*b*) and 3 c.c. of the potassium iodate solution (*a*) are measured into a beaker and then poured into the flask. Some glass beads are then added, and the flask stoppered and shaken for 5 minutes in the cold, no advantage being gained by heating it. The contents are then washed into a 250 or 500 c.c. flask and made up to the mark with water. 50 or 100 c.c. are now pipetted into a distilling flask, acidified with sulphuric acid, and the iodine so set free distilled into potassium iodide solution, and titrated with thiosulphate in the usual way. The following reactions take place:—

$$15Zn + 30KOH = 15Zn(OK)_2 + 15H_2$$
$$5KIO_3 + 15H_2 = 5KI + 15H_2O$$
$$5KI + KIO_3 + 3H_2SO_4 = 3K_2SO_4 + 3H_2O + 6I.$$

Therefore 6I correspond to 15Zn, or 1 gm. of iodine to 1·2876 gm. zinc.

---

[1] *J. S. C. I.*, 1886, **5**, 145.

[2] *Ibid.*, 1908, **27**, 450.

[3] *Z. a. C.*, 1890, **29**, 253.

A simpler method has been devised by A. R. Wahl,[1] but like many others it gives no protection against metallic iron, but this of course can be ascertained by other means.

It was found that when solid ferric sulphate is added to zinc dust suspended in a little cold water with exclusion of free acid, a reaction occurs with evolution of heat, and the zinc quickly and totally dissolves with formation of a clear greenish solution. A small residue remains consisting of lead and other impurities. The solution of the zinc takes place without any evolution of hydrogen, and the reaction is therefore represented by the equation—

$$Fe_2(SO_4)_3 + Zn = ZnSO_4 + 2FeSO_4.$$

When all has dissolved, it is only necessary to acidify the solution with sulphuric acid and titrate with permanganate to find the quantity of ferrous salt formed, and hence the quantity of metallic zinc in the sample under examination.

Preparation of Pure Ferric Sulphate.—500 gm. of pure ferrous sulphate are dissolved in as little water as possible, and to it are added 100 gm. of sulphuric acid and gradually 210 gm. of nitric acid (60 per cent.). On adding the nitric acid, torrents of nitrous gas are evolved, the solution acquiring a nearly black colour, which disappears again when the whole of the acid is added. The solution is evaporated on the water-bath until it becomes solid, when it is ground with alcohol in a mortar, put on a filter, and washed with alcohol until the filtrate is no longer acid. The product is then dried thoroughly on the water-bath to remove all alcohol, and the salt, which is a perfectly white powder, is kept in stoppered bottles for use.

Method of Procedure: About ½ gm. of zinc dust is put into a stoppered 250 c.c. flask and to it are added 25 c.c. of cold water. The mixture is agitated, and when the zinc is thoroughly suspended, 7 gm. of ferric sulphate are added. There is a gentle evolution of heat, and after shaking for a quarter of an hour the zinc will have completely dissolved, with the exception of a slight residue of impurities. 25 c.c of strong sulphuric acid are then added, and the flask is made up to the mark with water. 50 c.c. of this solution, after dilution with 50 c.c. of water, are titrated with standard permanganate.

From the quantity of the latter employed, the percentage of metallic zinc is at once found

Another method (by A. Fraenkel)[2] is as follows:—

One gm. of the sample is weighed into a dry stoppered 200 c.c. flask, mixed with 100 c.c. of potassium dichromate solution (30 gm. per litre) and 10 c.c. of 1 : 3 sulphuric acid, and agitated for 5 minutes. Another 10 c.c. of acid are then added, and the shaking continued for 10 or 15 minutes, when everything, except a small earthy residue, should be dissolved. The liquid is diluted to 500 c.c., and in 50 c.c. thereof the excess of dichromate is determined by introducing 10 c.c. of 10 per cent. potassium iodide and 5 c.c. of sulphuric acid, and titrating the liberated iodine with decinormal thiosulphate.

---

[1] *J. S. C. I.*, 1897, **16**, 15.

[2] *Analyst*, 1900, **25**, 279.

7. Zinc Oxide and Carbonate.

Benedikt and Cantor[1] show that zinc oxide and carbonate can be accurately titrated residually with standard acid and alkali, using methyl orange as indicator; and other zinc salts, using phenolphthalein. The oxide or carbonate is dissolved in excess of acid, and the excess determined by soda solution. Zinc salts are dissolved in water (50 c.c. to 0·1 gm. ZnO), phenolphthalein is added, and then standard soda solution to intense red colour. A few more c.c. of soda are then added, the mixture is boiled for some minutes, and the excess of soda titrated. If either free acid or zinc oxide is present in the zinc salt, it is neutralized in presence of methyl orange by alkali or acid, as the case may be.

[1] *Z. angew. C.*, 1888, 2, 236

PART VI.

SPECIAL APPLICATIONS OF THE VOLUMETRIC SYSTEM TO THE ANALYSIS OF ORGANIC SUBSTANCES.

ACETONE.

Dimethyl-Ketone $CO(CH_3)_2 = 58·048$.

ACETONE is an important constituent of wood-spirit and is largely used as a solvent in the manufacture of cordite, the insoluble cellulose hexanitrate being by its aid worked into a homogeneous mixture with the nitroglycerine. For such purposes the acetone must be free from high boiling constituents and especially from acid or acid-forming substances, which are injurious. The British Government specification[1] for acetone is as follows:—

"The liquid is to be genuine Acetone and must contain no other ingredients except small quantities of substances which are normal by-products of the manufacture of Acetone. It must be colourless and absolutely transparent, and when mixed with distilled water in any proportions it must show no turbidity. It must leave no residue when evaporated upon a boiling water-bath.

"The sp. gr. must not be greater than 0·800 at 15·5° C. compared with water at the same temperature.

"One cubic centimetre of a 0·10 per cent. solution in distilled water of pure permanganate of potash added to 100 cubic centimetres of the Acetone must retain its distinctive colour for not less than 30 minutes. This test is to be conducted at a temperature of 15·5° C.

"The Acetone is not to contain more than 0·002 per cent. of carbon dioxide, and is otherwise to be quite neutral."

The above stringent requirements ensure that only the middle fractions from the distillation of acetone from acetate of lime are supplied, and that the acetone is not contaminated with foreign matter, and contains no more than traces of any substances except ethyl methyl ketone, and only a small quantity of that.[2]

Commercial acetones may contain both basic bodies and acids. The basic bodies and strong acids may be determined by diluting a measured volume of the sample with an equal volume of boiled distilled water, adding 2 to 4 drops of a saturated solution of paranitrophenol in water, and titrating with standard acid or alkali solution. Weak acids may be detected and determined by mixing with water as before, boiling for 5 or 10 minutes, adding phenolphthalein and titrating with standard caustic alkali. Carbon dioxide is readily determined by adding water and phenolphthalein and titrating at once without boiling.

---

[1] This was kindly supplied by the Director of Propellant Supplies, Ministry of Munitions of War, in November 1918.

[2] Marshall "Acetone: its manufacture and purification," *J. S. C. I.*, 1904, **23**, 645.

Conroy[1] points out the importance of protecting from light all samples of acetone intended for testing.

Acetone may be determined by Messinger's method,[2] which depends upon the fact that when acetone is treated with iodine and potash iodoform and potassium acetate are formed. It is carried out as follows: –

25 c.c. of $^{N}/_{1}$ KOH and 1 to 2 c.c. of the sample (e.g. methyl alcohol) are measured into a stoppered 250 c.c. flask, the mixture well shaken, and allowed to stand for 5 to 10 minutes. $^{N}/_{5}$ iodine solution is then run in from a burette, drop by drop, vigorously shaking all the time, until the upper portion of the solution, after standing a minute, becomes quite clear. A few more c.c. of $^{N}/_{5}$ iodine are added, as an excess is essential. After shaking, the mixture is allowed to stand for 10 to 15 minutes and then 25 c.c. $^{N}/_{1}$ sulphuric acid are added. The excess of iodine thus liberated is then titrated with $^{N}/_{10}$ sodium thiosulphate solution and starch.

Let n be the c.c. of $^{N}/_{5}$ iodine required by the acetone (= volume added less half the volume of thiosulphate required), m be the c.c. of sample taken and then

$$\frac{n \times 0{\cdot}19334}{m} = \text{gm. of acetone per 100 c.c.}$$

This includes as acetone any aldehydes, etc., capable of yielding iodoform by this reaction.

Rakshit[3] has shown that a correction of 1·6 c.c. of $^{N}/_{10}$ iodine solution must be made for each c.c. of ethyl alcohol, and for each c.c. of methyl alcohol Goodwin[4] finds that the correction is 1 c.c. of iodine solution.

ANILINE.

$C_6H_5NH_2 = 93{\cdot}066.$

A process for determining aniline or its salts has been devised by M. François.[5] The method depends on the fact that if bromine water is added to an aniline solution, which contains a little soluble indigo as indicator, the bromine does not act on the indigo until all the aniline has been converted into tribrom-aniline.

Method of Procedure: The bromine water (5 gm. bromine in 1000 c.c. water) is standardized by means of an aqueous solution of aniline hydrochloride, which contains 1·392 gm. of the pure salt in 1000 c.c. (1 c.c. = 0·001 gm. aniline). The bromine water, if exposed to the air, is continually losing bromine; it is, therefore, essential to use a burette of such capacity that it contains enough bromine water for both the standardization and determination without refilling; to close the end of the burette with a plug of cotton wool; to find approximately the number of c.c. of bromine water required, and then in the final titration to add nearly the whole at once in order to avoid the slight loss of bromine which occurs when drops of the solution fall through the air. The method may be applied to solutions containing aniline or its hydrochloride, the presence of ammonium chloride does not vitiate the result, and finally, if the solution to be titrated contains mineral substances which would react with the bromine, the aniline may be liberated by potash and distilled in steam. The degree of dilution of the aniline solution does not influence the result.

---

[1] *J. S. C. I.*, 1900, **19**, 209.

[2] *Ber.*, 1888, **21**, 3666; also *J. S. C. I.*, 1889, **8**, 138.

[3] *Analyst*, 1916, **41**, 246.

[4] *J. A. C. S.*, 1920, **42**, 39.

[5] *J. Pharm.*, 1899, 521.

Another method devised by Reinhardt is described by Liebmann and Studer,[1] who use a slight modification of it for determining aniline or mixtures of aniline and *o*- and *p*-toluidines which are sometimes present in technical oils. Reinhardt accomplishes this by titration of the oil in hydrobromic acid solution by potassium bromate and bromide.

Aniline requires three molecules of bromine to form tribrom-aniline, whilst *o*- and *p*-toluidine only absorb two molecules.

Method of Procedure: Reinhardt prepares his standard solution by boiling 480 gm. of Br with 336 gm. of KOH (100 per cent.) and 1 litre of water for 2 to 3 hours, then dilutes to 9 litres.

Hypobromites should not be present.

To carry out the analysis, he dissolves 1·5 to 2 gm. of oil in 1000 c.c. of water and 100 c.c. of hydrobromic acid of 1·4 to 1·5 sp. gr. He adds his bromate solution until iodized starch-paper indicates the presence of free bromine.

The following equation gives him the result—

$$X + (VT - X)\frac{107}{93} \times \frac{3}{2} = A \text{ or } X = \frac{107}{45}VT - \frac{62}{45}A,$$

in which X means aniline, V the volume of bromate used, T its titer, and A the weight of oil used for analysis. Toluidine is found by difference. To determine the relative quantities of *o*- and *p*-toluidine, use is made of the property of *p*-toluidine and aniline to be precipitated from their hydrochloric acid solution by oxalic acid, whilst *o*-toluidine remains in solution.

160 gm. of the oil are dissolved in 106 gm. of HCl of 20° B., and the mixture is then added to a hot 10 per cent. solution of oxalic acid.

The solution will at first be clear. It has to stand for 48 hours. The oxalates, which will then have separated out, are filtered and washed three times with 25 c.c. of distilled water.

After decantation with hot dilute KOH (100 c.c. KOH 45° B., 200 c.c. H_2O), the oil is separated, weighed, and finally titrated by the bromine solution to find the amount of *p*-toluidine present.

Liebmann and Studer have adopted this method, with slight modifications, for determining the aniline and toluidine oils, and also for analysing the aniline salts. To prepare the standard solution, 16·7 gm.

---

[1] *J. S. C. I.*, 1899, **18**, 110.

of pure potassium bromate and 59·5 gm. of potassium bromide are dissolved in 1 litre of water, and standardized by titration with sodium thiosulphate, using potassium iodide and starch as indicator.

For aniline they have found that concentrated hydrochloric acid can be used as solvent instead of hydrobromic acid, but that the latter is essential when toluidines are present. Instead, however, of using ordinary hydrobromic acid, they found that by dissolving 100 gm. of potassium bromide in 100 c.c. of hot water, and 100 c.c. of hydrochloric acid, sp. gr. 1·18, an acid is obtained which gives accurate results.

For pure aniline 0·5 gm. of the oil, or about 0·6 gm. of salt, is dissolved in about 500 c.c. of water and 30 c.c. of pure hydrochloric acid of 1·18 sp. gr., and the standard solution added until a distinct excess of bromine is observable. The reaction grows slower at the end of the operation, but it is found that to wait for 2 minutes is quite sufficient to determine whether free bromine is present in solution or not. The excess of bromine is determined by titration with $^N/_{10}$ thiosulphate solution, using potassium iodide and starch as indicator, 6 c.c. of the thiosulphate corresponding to 1 c.c. of the bromate solution.

For aniline containing toluidine 0·5 gm. is dissolved in 32 c.c. of hydrobromic acid, prepared as above, and 500 c.c. of water, and the titration is carried out in the same way as with pure aniline. A number of analyses of aniline oil and salt and of mixtures of aniline oil with toluidine of known composition gave excellent results.

Another method has been adopted of carrying out Reinhardt's process for determining the aniline and toluidine in aniline oil, which depends on the bromination of these two amines by potassium bromate in hydrobromic acid solution.

An 8 per cent. solution of pure potassium bromate is prepared, the strength being determined by mixing 25 c.c. with 5 gm. of potassium iodide and 3 c.c. of 25 per cent. hydrobromic acid solution, and determining, by titration with standard thiosulphate, the iodine set free according to the equation: $KBrO_3 + 6HBr + 6KI = 3I_2 + 7KBr + 3H_2O$. One gm. of iodine corresponds to 0·21933 gm. of potassium bromate, that is, with 0·12225 gm. of aniline, or 0·1393 gm. of toluidine. About 1 gm. of the aniline oil is dissolved in about 60 gm. of 25 per cent. hydrobromic acid solution, and the bromate solution run in until the clear liquid above the bromide precipitate assumes a yellow coloration. Then, if a is the weight of oil taken, n the number of c.c. of bromate solution employed, t_a and t_t the amounts of aniline and toluidine respectively corresponding with 1 c.c. of the bromate solution, the percentage of aniline in the oil is given by: $100t_a(nt_t - a)/a(t_i - t_a)$, and that of the toluidine by $100t_t(a - nt_a)/a(t_t - t_a)$.

Aniline hydrochloride may be titrated direct by standard caustic alkali, using phenolphthalein or litmus (but not methyl orange) as indicator, as it acts exactly like an equivalent quantity of free hydrochloric acid. The presence of neutral ammonium salts has no detrimental effect.

AZO-DYES, NITRO- AND NITROSO-COMPOUNDS, Etc.

Dr. E. Knecht's Process.

THE powerful reducing properties of titanous chloride ($TiCl_3$) render this reagent capable of being put to a variety of uses in volumetric analysis. Thus, in addition to its uses in the volumetric determination of iron (and arsenic), it has been found available for the exact determination of several series of aromatic compounds, including the azo-compounds, the nitro and the nitroso-compounds. In all the cases hitherto observed, the reduction takes place in such a manner that each azo-group present requires (in accordance with theory) four equivalents, each nitro-group (NO_2) six equivalents, and each nitroso-group (NO) four equivalents of $TiCl_3$. Thus with benzene-azo-betanaphthol, the reaction takes place according to the following equation :-

$$C_6H_5N : N.C_{10}H_6OH + 4TiCl_3 + 4HCl =$$
$$C_6H_5NH_2 + C_{10}H_6(OH)(NH_2) + 4TiCl_4$$

with picric acid,

$$C_6H_2(OH)(NO_2)_3 + 18TiCl_3 + 18HCl =$$
$$C_6H_2(OH)(NH_2)_3 + 18TiCl_4 + 6H_2O$$

and with nitrosodimethylaniline,

$$C_6H_4 . N(CH_3)_2 . NO + 4TiCl_3 + 4HCl =$$
$$C_6H_4 . N(CH_3)_2 . NH_2 + 4TiCl_4 + H_2O.$$

In using titanous chloride for these determinations, it is essential that the reagent should be kept out of contact with the air, both in the storage vessel and in the burette, and for this purpose the arrangement shown in fig. 41 should be used.

The most suitable strength of titanous chloride for titrating is a 1 per cent. solution, obtained by diluting the commercial product with water. For this purpose 50 c.c. of the commercial 20 per cent. solution are first mixed with an equal volume of strong hydrochloric acid and boiled for a few minutes in a flask. The solution is then made up to a litre with distilled water which has been previously boiled. The method of ascertaining its strength is shown on page 241. When two or more titrations agree, the iron value per c.c. of the titanous chloride solution is easily calculated.

In case the azo-compound under examination is not precipitated by dilute hydrochloric acid, it may be titrated directly, its own intense colour serving as indicator.

For the titrations a solution of 0·5 gm. of the dyestuff is made up to 500 c.c. with distilled water, and of this 100 c.c. are taken. The following example may serve as an illustration :

CRYSTAL SCARLET 6R. $C_{20}H_{12}N_2S_2O_2Na_2 + 7H_2O$ (colouring matter from alpha naphthylamine and G. salt).

0·5 gm. of the dyestuff was dissolved in distilled water and the solution made up to 500 c.c. Of this, 100 c.c. were measured out into a conical flask and, after adding about 10 c.c. concentrated hydrochloric acid, boiled for about a minute. This amount required 22·6 c.c. of titanous chloride solution.

The calculation is as follows :—

$$1 \text{ c.c. } TiCl_3 = 0{\cdot}00158 \text{ gm. Fe}$$

and 502 gm. colour require by theory 224 gm. Fe.

$$\therefore \frac{0{\cdot}00158 \times 22{\cdot}6 \times 502}{224} = 0{\cdot}08002 \text{ gm. colour.}$$

			Calc.
And 1 gm. contains 0·8002 or	80·02	per cent.	79·96
Water of cryst. at 140° C. =	19·96	„	20 04
Total	99·98		100·00

In the case of dyestuffs which, like the majority of the benzidine derivatives, are thrown out of solution by hydrochloric acid, the reaction is too slow and the end of the reaction often not sufficiently sharp to admit of exact determinations. In such cases it is best to run an excess of titanous chloride solution into the boiling solution of the dyestuff, taking the precaution to keep a gentle current of carbonic acid passing into the flask by a tube which almost touches the surface of the liquid. The reduction will usually be completed in less than 2 minutes, when the flask is cooled under the tap, without, however, interrupting the current of carbonic acid. When cold, the excess of titanous chloride is determined as already described by running in iron alum solution of known strength (but preferably nearly equivalent to that of the titanous chloride solution) until a drop taken out and spotted on potassium sulphocyanide solution just shows a red colour. By subtracting the number of c.c.'s of the iron alum solution (or their equivalent in titanous chloride, should the two solutions not be of equal strength) from the total number of c.c.'s of titanous chloride run in, the exact amount of the latter used up in the reduction of the dyestuff is arrived at.

The following example will serve to illustrate the application of the indirect method:—

BENZOPURPURIN 4 B, $C_{34}H_{26}N_6S_2O_6K_2 + 4\frac{1}{2} H_2O$ (potassium salt of the colouring matter from toluidine and naphthionic acid).

0 5 gm. of the dyestuff is dissolved in distilled water, and the solution made up to 500 c.c. Of this 100 c.c. were measured into a conical flask and heated to the boil. 10 c.c. concentrated hydrochloric acid and 50 c.c titanous chloride solution were then added, carbonic acid being passed into the flask. The contents of the flask were now boiled for about a minute, when complete reduction took place, and, after cooling, the solution required 22·9 c.c. iron alum (equivalent to 21·0 c.c. titanous chloride). The excess of titanous chloride added was therefore 21·0 c.c., and this, subtracted from 50, gives 29·0 c.c. titanous chloride as having been used for the reduction. The calculation is as follows:—

$$1 \text{ c.c. } TiCl_3 - 0{\cdot}001845 \text{ gm. Fe}$$

and 756 gm. colour require by theory 448 gm. Fe.

$$\therefore \frac{0{\cdot}001845 \times 29 \times 756}{448} = 0{\cdot}09026 \text{ gm. colour.}$$

	Examd	Calc
And 1 gm. contains 0·9026 or	90·26 per cent.	90·33 per cent.
Water of cryst	9·63	9·67
	99·89	100·00

For the determination of picric acid and other nitro-compounds, it is also necessary to employ the indirect method, the end of the reaction not being perceptible by the direct method.

CARBON DISULPHIDE AND THIOCARBONATES.

$CS_2 = 76{\cdot}12.$

FOR the purpose of determining carbon disulphide in the air of soils, gases, or in thiocarbonates, Gastine[1] has devised the following process:—

---

[1] *Compt. Rend.*, 1884, **98**, 1588.

The gas or vapour to be tested is carefully dried, and then passed through a concentrated solution of recently fused potassium hydroxide in absolute alcohol. The presence of even traces of water seriously diminishes the delicacy of the reaction. The alcoholic solution is afterwards neutralized with acetic acid, diluted with water, and tested for xanthic acid by adding copper sulphate.

In order to determine the distribution of carbon disulphide introduced into the soil, 250 c.c. of the air in the soil is drawn by means of an aspirator through sulphuric acid, and then through bulbs containing the alcoholic potash. For quantitative determinations, a larger quantity of air must be used, and the xanthic acid formed is determined by means of the reaction $2C_3H_6OS_2 + I_2 = 2C_3H_5OS_2 + 2HI$. The alkaline solution is slightly acidified with acetic acid, mixed with excess of sodium bicarbonate, and titrated in the usual way with a solution of iodine, containing 1·68 gm. per litre, 1 c.c. of which is equivalent to 1 mgm. of carbon disulphide.

To apply this method to thiocarbonates, about 1 gm. of the substance, together with about 10 c.c. of water, is introduced into a small flask and decomposed by a solution of zinc or copper sulphate, the flask being heated on a water-bath, and the evolved carbon disulphide passed, first through sulphuric acid, and then into alcoholic potash. In the case of gaseous mixtures of carbon disulphide, nitrogen, hydrogen sulphide, carbonic anhydride, carbonic oxide, and water vapour the gas is passed through a strong aqueous solution of potash, then into sulphuric acid, and finally into alcoholic potash. The thiocarbonate formed in the first flask is decomposed by treatment with copper or zinc sulphate as above, and the xanthic acid obtained is added to that formed in the third flask, and the whole titrated with iodine.

Harding and Doran's Method.[1] **For CS_2 in Benzene.** A known volume of the benzene is shaken in a separating funnel with a solution of potassium hydroxide in absolute alcohol. After standing half an hour, the mixture is extracted several successive times with water containing a little alkali, about 40 c.c. of water and 1 c.c. of alcoholic potassium hydroxide solution being used each time. The aqueous extracts are diluted to a known volume, and a portion is acidified with acetic acid and precipitated by the addition of a distinct excess of standard cupric acetate solution. The precipitate is stirred for about 10 minutes, collected on a filter, and washed with four quantities of water, using 15 c.c. each time. About 3 gm. of potassium iodide are added to the filtrate, and the liberated iodine is titrated with a sodium thiosulphate solution whose strength in terms of cupric acetate is known. The authors find that the ratio of CuO to CS_2 is 1 to 1·927. This ratio approaches nearest to that between cupric oxide and carbon disulphide in cupric xanthate, which has the formula $(CS . OC_2H_5S)_2Cu$, and in which the ratio is 1 to 1·9126; this tends to strengthen the belief that the compound formed is cupric xanthate.

For CS_2 in Illuminating Gas.—The method consists in passing the gas through a meter, absorbing the carbon dioxide with potassium hydroxide, drying the gas by means of concentrated sulphuric acid, and absorbing the carbon disulphide in an alcoholic solution of potassium hydroxide. The water in the meter must be saturated previously with gas, and about 2 cubic feet of the latter are employed for the determination, the gas being allowed to flow at the rate of 0·5 cubic foot per hour. The xanthate solution obtained is boiled to expel absorbed gases, cooled, acidified with acetic acid, and precipitated by the addition of standard cupric acetate solution. The determination is then carried out as described above.

---

[1] *J. A. C. S.*, 1907, **29**, 1476.

For a critical examination of the various methods for the determination of carbon disulphide, see Spielmann and Jones, *J. S. C. I.*, 1919, **38**, 185 T.

FORMALDEHYDE.

H.CHO = 30·016.

THIS substance is met with in commerce in the form of a 40 per cent. (by volume) aqueous solution ("Formalin") containing usually from 36 to 38 per cent. by weight of formaldehyde. Solutions containing more than 40 per cent. of formaldehyde polymerize spontaneously to paraformaldehyde.

For the purpose of determining formaldehyde in solutions the following processes are employed:

LEGLER'S METHOD: This method is based on the following reaction:—

$$6CH_2O + 4NH_3 = (CH_2)_6N_4 + 6H_2O.$$

From this we find that 1 part of ammonia represents 2·6432 parts of formaldehyde. Hexamethylene-tetramine, $N_4(CH_2)_6$ is formed as a condensation product.

METHOD OF PROCEDURE: The solution to be tested, if slightly acid, is shaken with calcium carbonate, and 5 c.c. of the clear supernatant liquid are treated with 100 c.c. of $^N/_2$ ammonium hydroxide and kept for a day at the ordinary temperature in a closed vessel. The excess of ammonium hydroxide is then titrated by $^N/_2$ HCl, using litmus as indicator.

Let *n* c.c. of $^N/_2$ HCl be required.

Then (100 − *n*) c.c. of $^N/_2$ ammonia have been used.

This contains (100 − *n*) × 0·008517 gm. NH_3 and equals (100 − *n*) × ·008517 × 2·6432 gm. formaldehyde in 5 c.c., or (100 − *n*) × 0·4502 gives grams formaldehyde in 100 c.c.

R. Lessing states (in Thorpe's *Dict. of Applied Chemistry*) that Legler's method gives low results: also that "For impure concentrated solutions the method of Blank and Finkenberger may be employed".

The error of the method is due to (1) loss of ammonia, (2) tendency of the weak base hexamethylenetetramine to combine with acid, and (3) liability of the base to dissociate into formaldehyde and ammonia.

BLANK AND FINKENBERGER'S METHOD[1]: It is based on the oxidation of formic aldehyde to formic acid by peroxide of hydrogen in alkaline solution, and titration of the excess of alkali.

---

[1] *Berichte*, 1898, 2979, also *Analyst*, 1899, **24**, 92.

METHOD OF PROCEDURE: 3 gm. of the solution of formic aldehyde under examination (or 1 gm. in the case of a solid) are weighed out carefully and placed in a tall conical flask containing 25 c.c. of twice-normal soda (30 c.c. when the concentration of the formic aldehyde is greater than 45 per cent). The mixture is then immediately treated with 50 c.c. of peroxide of hydrogen at from 2·5 to 3 per cent. strength; in the case of the peroxide having an acid reaction, the acidity should be determined and deducted from the final result. The peroxide of hydrogen must be added gradually (taking about 3 minutes) by means of a funnel; after 2 or 3 minutes the funnel is rinsed with water, and the excess of alkali is titrated with a twice-normal solution of sulphuric acid; in very exact analyses the water used for rinsing should be boiled first to drive off any carbonic acid. Litmus is used as an indicator.

With solutions containing less than 30 per cent. of formic aldehyde the mixture should be allowed to stand for about 10 minutes after the addition of the peroxide of hydrogen, for the reaction to be complete.

The volume of standard alkali used, multiplied by 6, gives the formaldehyde in 1 gm. of the solid or, multiplied by 2, in 3 gm. of the solution.

The reaction takes place with the disengagement of a considerable amount of heat and production of froth.

Experiments on other aldehydes did not give satisfactory results.

A further method, especially applicable to dilute solutions, is furnished by R. Orchard.[1] It is based on the reaction of formaldehyde with ammoniacal silver solution, and in this process it is arranged quantitatively, and can be carried out either by weight or the residual silver found volumetrically.

METHOD OF PROCEDURE: In the actual experiments 10 c.c. of an approximately 0·1 per cent. solution of formaldehyde were added to 25 c.c. $^{N}/_{10}$ silver nitrate, 10 c.c. of dilute ammonia (1 of 0·88 solution to 50 of water) added, and the whole boiled in a conical flask attached to a reflux condenser. The precipitate, after filtration and washing, was ignited and weighed as metallic silver, and as a check the excess of silver was determined in the filtrate as silver chloride. As the first experiments showed that the reduction was incomplete after boiling for half an hour, the boiling was continued for 4 hours. In order to ascertain if any loss took place during boiling, a duplicate determination was made, in which a bottle with a tied-down stopper, heated in a water-bath, was employed. The actual results obtained were in the first case 0·01038 gm. formaldehyde, and in the second 0·0104 gm., consequently there was practically no loss.

In the calculation, as one molecule of CH_2O reduces two molecules of Ag_2O, the weight of the precipitated silver multiplied by the factor 0·0696 gives the weight of the formaldehyde, and 1 c.c. $^{N}/_{10}$ silver nitrate corresponds to 0·00075 gm. formaldehyde; it is, therefore, possible to determine extremely small quantities by this process.

---

[1] *Analyst*, 1897, **22**, 4.

A number of experiments were carried out on the determination of formaldehyde by G. Romijn.[1] The methods of Legler, Brochet, and Cambier were studied, and the results obtained with them compared with those given by two new methods described below. For this purpose four aqueous solutions were prepared containing in 500 c.c.: (1) 2·075 gm. of formalin; (2) 2·075 gm. of formalin + 1·3 gm. acetaldehyde; (3) 2·075 gm of formalin + 0·355 gm. of acetone; (4) 2·075 gm. of formalin + 1 gm. of benzaldehyde.

IODIMETRIC METHOD.—10 c.c. of the aldehyde solution are mixed with 25 c.c. of decinormal iodine solution, and sodium hydrate added drop by drop until the liquid becomes clear yellow. After 10 minutes hydrochloric acid is added to liberate the uncombined iodine, which is then titrated back with standard thiosulphate. Two atoms of iodine are equivalent to 1 molecule of formaldehyde. The amount of iodine taken up multiplied by 0·1183 gives the amount of formaldehyde. The results obtained with the first solution showed that the formalin used contained (1) 37·38 and (2) 37·40 per cent. of formaldehyde.

With the second solution a certain amount of iodoform was produced, and the results were too low. With the third solution the acetone was entirely converted to iodoform, and in the fourth solution the benzaldehyde was partially oxidized. Hence this method, though suitable for the valuation of pure formaldehyde, does not give correct results in the presence of other aldehydes.

POTASSIUM CYANIDE METHOD.—This is based on the fact that formaldehyde combines with potassium cyanide. The addition product reduces silver nitrate in the cold. But if the silver nitrate be acidified with nitric acid before the addition of the aldehyde cyanide mixture, no precipitate results if the aldehyde in the latter be in excess. If, on the other hand, the potassium cyanide is in excess, 1 molecule of potassium cyanide is left in combination with 1 molecule of the formaldehyde, while the excess precipitates silver cyanide from the silver nitrate solution.

10 c.c. of decinormal silver nitrate, acidified with nitric acid, are mixed with 10 c.c. of potassium cyanide solution (prepared by dissolving 3·1 gm. of the 96 per cent. salt in 500 c.c.), the whole diluted to 500 c.c., filtered, and 25 c.c. of the filtrate titrated by Volhard's method (p. 150). The difference between this blank result and that obtained by titrating the filtrate after the addition of the aldehyde solution gives the amount of standard sulphocyanide corresponding to the silver not precipitated by the excess of potassium cyanide. From this the amount of formaldehyde can be calculated. With solution 1 the results showed 37·39 and 37·67 per cent. of formaldehyde in the formalin. With solution 2, if the titration was made immediately after shaking, only the formaldehyde had combined, but if left for some time the acetaldehyde also began to combine, and erroneous results were obtained. Solutions 3 and 4 gave correct results, even after standing for 30 minutes.

HYDROXYLAMINE METHOD (Brochet and Cambier).[3]—This gave satisfactory results with pure formaldehyde, but quite irregular figures with the other three solutions.

LEGLER'S METHOD.[2]—The four solutions were made more concentrated in order to lessen the difficulty of observing the end-reaction. In each case the correct amount of formaldehyde was found, but the author does not consider the method so accurate as the others.

---

[1] *Z. a. C.*, 1897, **36**, 18-24.

[3] *Compt. Rend.*, 1895, **120**, 449.

[2] *Berichte*, 1883, **16**, 1335.

Acetaldehyde.—A method originally proposed by Reiter[1] has been modified by Roques with good results.

METHOD OF PROCEDURE: A sodium sulphite solution is made by dissolving 12·6 gm. of anhydrous sodium sulphite in 400 c.c. of water, adding 100 c.c. of normal sulphuric acid, diluting to 1000 c.c. with alcohol of 96 per cent., and filtering after 24 hours. A convenient quantity of the alcoholic solution of aldehyde to be examined is placed in a 100 c.c. stoppered flask, mixed with 50 c.c. of the sulphite solution and made up to 100 c.c. with alcohol of 50 per cent. A second quantity of 50 c.c. of the sulphite solution is placed in a similar flask, and made up to 100 c.c. with the same alcohol. After heating to 50° C. at least 4 hours, 50 c.c. are withdrawn from each flask, and the sulphurous acid determined by means of $^{N}/_{10}$ iodine solution; the difference is the quantity of sulphurous acid that is in combination with the aldehyde;

1 c.c. of $^{N}/_{10}$ iodine = 0·0022 gm. of aldehyde.

If the liquid to be examined contains less than 1 per cent. of aldehyde the sulphite solution must be diluted; for 0·5 per cent., it should be diluted with an equal volume of alcohol of 50 per cent., and $^{N}/_{20}$ iodine should be used; for 0·1 per cent., the sulphite should be diluted with alcohol of 50 per cent. to 10 times its ordinary volume, and centinormal iodine solution should be used.

A Volumetric Method for the Determination of various Aldehydes has been devised by M. Ripper.[2]—The method is based on the combination of alkali bisulphites with aldehydes. 25 c.c. of the solution to be examined, which should not contain more than ½ per cent. of the aldehyde, are run into 50 c.c. of a solution of potassium bisulphite containing 12 gm. $KHSO_3$ per litre, placed in a 150 c.c. flask, which is then securely corked, and allowed to stand for a quarter of an hour. During this time another 50 c.c. of the potassium bisulphite solution are titrated with $^{N}/_{10}$ iodine. The excess of bisulphite added to the aldehyde solution is then determined with the same iodine solution, and from the difference the amount of aldehyde present is calculated.

The amount of the aldehyde is obtained by the formula—

$$A = \frac{I \times \frac{M}{2}}{126{\cdot}92} = \frac{I \times M}{253{\cdot}51}$$

in which A represents the amount of aldehyde, I the iodine corresponding to the combined sulphurous acid, and M the molecular weight of the aldehyde in question.

From this the following factors are obtained:—

Formaldehyde = I × 0·1179
Acetaldehyde = I × 0·1729
Benzaldehyde = I × 0·4166
Vanillin = I × 0·5974.

The method is said to yield reliable results in all cases in which the aldehyde is soluble in water, or can be brought into solution by the addition of a little alcohol.

---

[1] *J. S. C. I. abstr.*, 1897, **16**, 606.

[2] *Monatshefte f. Chem.* 1900, **21**, 1079.

In the case of the four aldehydes mentioned above, test analyses are described in detail to show that the results are in close agreement with those obtained by recognized reliable methods.

Solutions of potassium bisulphite stronger than the above should not be employed, as the larger quantities of hydriodic acid formed would exert a reducing action on the sulphuric acid formed. The use of alcohol to dissolve the aldehyde should also be avoided as far as possible, as even relatively small quantities of alcohol (upwards of 5 per cent.) interfere with the iodide of starch reaction. With the very dilute solutions of aldehyde used, however, a very small addition of alcohol will be sufficient in most cases.

GLYCEROL.

(GLYCERIN.)

$$C_3H_5(OH)_3 = 92{\cdot}064.$$

Glycerol in aqueous solution may be determined by means of standard permanganate, as first suggested by Wanklyn, improved by him and Fox, and further elaborated by Benedikt and Zsigmondy.[1] The glycerol becomes oxidized to oxalic acid and carbon dioxide thus:—

$$C_3H_8O_3 + 3O_2 = H_2C_2O_4 + CO_2 + 3H_2O.$$

Method of Procedure: 0·2 to 0·3 gm. of the concentrated glycerin (or a corresponding amount of dilute glycerin, as calculated approximately from its sp. gr.) is mixed with 250 c.c. of water in a large flask, 10 gm. of solid KOH added, and a 5 per cent. solution of potassium permanganate run in at the ordinary temperature until the liquid ceases to be green and becomes blue or black in colour. Finely powdered permanganate may be used in place of its solution. The mixture is then boiled, when hydrated manganese dioxide is precipitated and the solution becomes red.

Sulphurous acid or sodium sulphite solution is then cautiously added, drop by drop, until the liquid just becomes colourless, and the solution filtered through a filter large enough to take at least half the liquid at one time. The precipitate is thoroughly washed with hot water. The last washings sometimes become turbid owing to the formation of manganese hydroxide, but the turbidity disappears on acidifying with acetic acid before precipitating with calcium chloride. 10 c.c. of a 10 per cent. solution of calcium chloride are then added to the boiling liquid, and, after digesting for some time, the precipitate is filtered off, and washed thoroughly with hot water. The filter is pierced and the precipitate washed into a porcelain dish. The neck of the funnel is then plugged and the filter filled with dilute sulphuric acid. After standing for 5 or 10 minutes this is allowed to run into the dish and the filter washed with water. Acid is added to the contents of the dish in quantity sufficient to bring the total amount used to 10 c.c. of concentrated acid, the liquid is diluted and about 200 c.c. brought to a temperature of about

---

[1] *Chem. Zeit.*, 1885, **9**, 975, and *J. S. C. I.*, 1885, **4**, 610.

60° C., and $^N/_{10}$ permanganate run in gradually from a burette until a distinct pink coloration remains on stirring.

$$1 \text{ c.c. of } {}^N/_{10} \text{ permanganate} = 0{\cdot}0045 \text{ gm. } H_2C_2O_4$$
$$= 0{\cdot}0046 \text{ gm. glycerol.}$$

In the above method excess of sulphurous acid must be carefully avoided, as in presence of hydrated manganese dioxide it destroys oxalic acid. Sodium sulphite, the use of which was suggested by Allen, gives sulphurous acid when acidified with acetic acid and this SO_2, in presence of the small quantity of manganese dioxide which has passed through the filter, causes a loss of oxalic acid.

Herbig has, therefore, suggested the use of hydrogen peroxide in place of sulphite. Mangold[1] reported favourably on the method and recommends the following procedure:—

To 0·2-0·4 gm. of glycerol, dissolved in 300 c.c. of water containing 10 gm. KOH, as much of a solution containing 5 per cent. potassium permanganate is added as will correspond with 1·5 times the theoretical quantity of glycerol (1 gm. glycerol requires 6·87 gm. of permanganate). The operation is conducted in the cold and the solution must be agitated on adding the permanganate. After standing for about half an hour at ordinary temperature, sufficient hydrogen peroxide is added completely to decolorize the liquid. The whole is now made up to 1000 c.c., well shaken, and 500 c.c. filtered off through a dry filter. After heating the filtrate for half an hour to destroy all hydrogen peroxide, and cooling to about 60°, sulphuric acid is added and the liquid titrated with permanganate as described above. The method was found to give accurate results even in the presence of 90 per cent. of butyric acid.

Another oxidation method of determination of glycerol is the Potassium Dichromate method of O. Hehner (see below).

The Acetin Method of Benedikt and Cantor[2] is based on the quantitative conversion of glycerol into triacetin (glyceryl triacetate) when heated with acetic anhydride, thus:—

$$C_3H_5(OH)_3 + 3(C_2H_3O)_2O = C_3H_5(O.C_2H_3O)_3 + 3C_2H_4O_2.$$

The triacetin is then saponified with sodium hydroxide solution, and the amount of the latter used gives a measure of the glycerol. Lewkowitsch has shown that this method gives closely concordant results in the case of moderately pure "crude glycerins," and recommends its adoption in all cases in which the glycerol is first isolated in a fairly pure state as in its determination in fats and oils (see below).

Owing to the large commercial interests involved, the valuation of crude glycerin is of such importance that in 1911 International Standard Methods of Analysis were adopted. These will now be given in full and verbatim.

METHODS OF CRUDE GLYCERINE ANALYSIS.

Recommended by the International Committees.

Sampling.—The most satisfactory method available for sampling crude glycerine liable to contain suspended matter, or which is liable to deposit salt on settling, is to have the glycerine sampled by a mutually approved sampler as soon as possible after it is filled into drums, but in any case before any separation of salts has taken place. In such cases he shall sample with a sectional sampler, then seal the drums, brand them with a number for identification, and keep a record of the brand number. The presence of any visible salt or other suspended matter is to be noted by the sampler, and a report of same made in his certificate, together with the temperature of the glycerine. Each drum must be sampled. Glycerine which has deposited salt or other matters cannot be accurately sampled from the drums, but an approximate sample can be obtained by means of the sectional sampler, which will allow a complete vertical section of the glycerine to be taken, including any deposit.

---

[1] *J. S. C. I.*, 1891, **10**, 803.

[2] *Ibid.*, 1888, **7**, 696, and 1889, **8**, 6.

Analysis.—1. Determination of Free Caustic Alkali.—Weigh 20 gm. of the sample into a 100 c.c. flask, dilute with approximately 50 c.c. of freshly-boiled distilled water, add an excess of neutral barium chloride solution and 1 c.c. of phenolphthalein solution, make up to the mark and mix. Allow the precipitate to settle, draw off 50 c.c. of the clear liquid, and titrate with normal acid ($N/_1$). Calculate to percentage of Na_2O existing as caustic alkali.

2. **Determination of Ash and Total Alkalinity.**—Weigh 2 to 5 gm. of the sample in a platinum dish, burn off the glycerine over a luminous Argand burner or other source of heat giving a low flame temperature, the temperature being kept low to avoid volatilization and the formation of sulphides. When the mass is charred to the point that water will not become coloured by soluble organic matter, lixiviate with hot distilled water, filter, wash, and ignite the residue in the platinum dish. Return the filtrate and washings to the dish, evaporate, and carefully ignite without fusion. Weigh the ash.

Dissolve the ash in distilled water and titrate total alkalinity, using as indicator methyl orange cold or litmus boiling.

3. **Determination of Alkali present as Carbonate.** Take 10 gm. of the sample, dilute with 50 c.c. distilled water, add sufficient $N/_1$ acid to neutralize the total alkali found at (2), boil under a reflux condenser for 15 to 20 minutes, wash down the condenser tube with distilled water, free from carbon dioxide, and titrate back with $N/_1$ NaOH using phenolphthalein as indicator. Calculate the percentage of Na_2O. Deduct the Na_2O found in (1). The difference is the percentage of Na_2O existing as carbonate.

4. **Alkali combined with Organic Acids.** The sum of the percentages of Na_2O found at (1) and (3) deducted from the percentage found at (2) is a measure of the Na_2O or other alkali combined with organic acids.

5. **Determination of Acidity.**—Take 10 gm. of the sample, dilute with 50 c.c. of distilled water free from carbon dioxide, and titrate with $N/_1$ NaOH and phenolphthalein. Express in terms of Na_2O required to neutralize 100 gm.

6. **Determination of Total Residue at 160° C.**—For this determination the crude glycerine should be slightly alkaline with Na_2CO_3 not exceeding the equivalent of 0·2 per cent. Na_2O, in order to prevent loss of organic acids. To avoid formation of polyglycerols this alkalinity must not be exceeded.

Preparation of Glycerine.—10 gm. of the sample is weighed into a 100 c.c. flask diluted with water and the calculated quantity of N/1 HCl or Na_2CO_3 added to give the required degree of alkalinity. The flask is filled to 100 c.c., the contents mixed, and 10 c.c. measured into a weighed petrie or similar dish 2·5 in. diameter and 0·5 in. deep, which should have a flat bottom. In the case of crude glycerines abnormally high in organic residue a less quantity is to be evaporated, so that the weight of organic residue does not materially exceed 30 to 40 mgm.

Evaporation of the Glycerine.—The dish is placed on a water-bath (the top of the 160° oven acts equally well) until most of the water has evaporated. From this point the evaporation is effected in the oven. Satisfactory results are obtained in an oven measuring 12 in. cube, having an iron plate ⅜ in. thick lying on the bottom to distribute the heat. Strips of asbestos millboard are placed on a shelf half-way up the oven. On these strips the dish containing the glycerine is placed.

If the temperature of the oven has been adjusted to 160° C with the door closed, a temperature of 130° to 140° can be readily maintained with the door partially open, and the glycerine, or most of it, should be evaporated off at this temperature. When only a slight vapour is seen to come off, the dish is removed and allowed to cool.

An addition of 0·5 to 1 c.c. of water is made, and by a rotary motion the residue brought wholly or nearly into solution. The dish is then allowed to remain on a water-bath or top of the oven until the excess water has evaporated and the residue is in such a condition that on returning to the oven at 160° C. it will not spit. The time taken up to this point cannot be given definitely, nor is it important. Usually two to three hours is required. From this point, however, the schedule of time must be strictly adhered to. The dish is allowed to remain in the oven, the temperature of which is carefully maintained at 160° C. for one hour, when it is removed, cooled, the residue treated with water, and the water evaporated as before. The residue is then subjected to a second baking of one hour, after which the dish is allowed to cool in a desiccator over sulphuric acid and weighed. The treatment with water, etc., is repeated until a constant loss of 1 to 1·5 mgm. per hour is obtained.

Corrections to be applied to the weight of the Total Residue.—In the case of acid glycerine a correction must be made for the alkali added. 1 c.c. N/1 alkali represents an addition of 0·022 gm. In the case of alkaline crudes a correction should be made for the acid added. Deduct the increase in weight due to the conversion of the NaOH and Na_2CO_3 to NaCl. The corrected weight, multiplied by 100, gives the percentage of **total residue at 160° C.**

Preserve the total residue for the determination of the non-volatile acetylizable impurities.

7. **Organic Residue.**—Subtract the ash from the total residue at 160° C. Report as organic residue at 160° C. (Note—It should be noted that alkaline salts of organic acids are converted to carbonates on ignition and that the CO_3 radicle thus derived is not included in the organic residue.)

8. **Moisture.**—This test is based on the fact that glycerine can be completely freed from water by allowing it to stand *in vacuo* over sulphuric acid or phosphoric anhydride.

2 to 3 gm. of very pure bulky asbestos freed from acid-soluble material, which has been previously dried in a water oven, is placed in a small stoppered weighing bottle of about 15 c.c. capacity. The weighing bottle is kept in a vacuum desiccator furnished with a supply of concentrated sulphuric acid, under a pressure equivalent to 1 to 2 mm. of mercury, until constant in weight. From 1 to 1·5 gm. of the sample is then carefully dropped on the asbestos in such a way that it will be all absorbed. The weight is again taken and the bottle replaced in the desiccator under 1 to 2 mm. pressure until constant in weight. At 15° C. the weight is constant in about 48 hours. At low temperatures the test is prolonged.

The sulphuric acid in the desiccator must be frequently renewed.

ACETIN PROCESS.

This process is the one agreed upon as giving results nearer to the truth on crudes in general and is the process to be used (if applicable) whenever only one method is employed. On pure glycerines the results are identical with those of the bichromate process. For the application of this process the crude glycerine should not contain over 50 per cent. water.

Re-Agents Required.—(A) **Best Acetic Anhydride.**—This should be carefully selected. A good sample must not require more than 0·1 c.c. normal NaOH for saponification of the impurities when a blank is run on 7·5 c.c. Only a slight colour should develop during digestion of the blank.

(B) **Pure Fused Sodium Acetate.**—The purchased salt is again completely fused in a platinum, silica, or nickel dish, avoiding charring, powdered quickly, and kept in a stoppered bottle or in a desiccator. It is most important that the sodium acetate be anhydrous.

(C) **A Solution of Caustic Soda for Neutralizing, of about $N/_1$ strength, free from Carbonate.**—This can be readily made by dissolving pure sodium hydroxide in its own weight of water (preferably water free from carbon dioxide) and allowing to settle until clear, or filtering through an asbestos or paper filter. The clear solution is diluted with water free from carbon dioxide to the strength required.

(D) **$N/_1$ Caustic Soda, free from Carbonate.** Prepared as above and carefully standardized.

Some caustic soda solutions show a marked diminution in strength after being boiled; such solutions should be rejected.

(E) **$N/_1$ Acid.**—Carefully standardized.

(F) **Phenolphthalein Solution.**—0·5 per cent. phenolphthalein in alcohol and neutralize.

Method of Procedure: Into a narrow mouthed flask (preferably round bottomed), capacity about 120 c.c., which has been thoroughly cleaned and dried, weigh accurately and as rapidly as possible 1·25 to 1·5 gm. of the glycerine. Add first about 3 gm. of the anhydrous sodium acetate, then 7·5 c.c. of the acetic anhydride, and connect the flask with an upright Liebig condenser. For convenience the inner tube of this condenser should not be over 50 cm. long and 9 to 10 mm. inside.

The flask is connected to the condenser by either a ground glass joint (preferably) or a rubber stopper. If a rubber stopper is used it should have had a preliminary treatment with hot acetic anhydride vapour.

Heat the contents and keep just boiling for one hour, taking precautions to prevent the salts drying on the sides of the flask.

Allow the flask to cool somewhat and through the condenser tube add 50 c.c. of the carbon dioxide-free distilled water heated to about 80° C., taking care that the flask is not loosened from the condenser. The object of cooling is to avoid any sudden rush of vapours from the flask on adding the water, and to avoid breaking the flask. Time is saved by adding the water before the contents of the flask solidify, but the contents may be allowed to solidify and the test proceeded with the next day without detriment. The contents of the flask may be warmed to, but must not exceed, 80° C. until the solution is complete except a few dark flocks representing organic impurities in the crude. By giving the flask a rotatory motion, solution is more quickly effected. Cool flask and contents without loosening from condenser. When quite cold wash down the inside of the condenser tube, detach the flask, wash off stopper or ground glass connection into the flask, and filter contents of flask through an acid washed filter into a Jena glass flask of about 1 litre capacity. Wash thoroughly with cold distilled water free from carbon dioxide. Add 2 c.c. of phenolphthalein solution (F), then run in a caustic solution (C) or (D) until a faint pinkish yellow colour appears throughout the solution. This neutralization must be done most carefully; the alkali should be run down the sides of the flask, the contents of which are kept rapidly swirling with occasional agitation or change of motion until the solution is nearly neutralized, as indicated by the slower disappearance of the colour developed locally by the alkali running into the mixture. When this point is reached the sides of the flask are washed down with carbon-dioxide-free water and the alkali subsequently added drop by drop, mixing after each drop until the desired tint is obtained.

Now run in from a burette 50 c.c. or a calculated excess of $N/_1$ NaOH (D), and note carefully the exact amount. Boil gently for 15 minutes, the flask being fitted with a glass tube acting as a partial condenser. Cool as quickly as possible and titrate excess of NaOH with $N/_1$ acid (E) until the pinkish yellow, or chosen end-point colour just remains. A further addition of the indicator at this point will cause a return of the pinkish colour; this must be neglected, and the first end-point taken.

From the $N/_1$ NaOH consumed calculate the percentage of glycerol after making the correction for the blank test described below.

1 c.c. of $N/_1$ NaOH = 0·03069 gm. of glycerol.

The coefficient of expansion for normal solutions is approximately 0·00033 per c.c. for each degree C. A correction should be made on this account if necessary.

Blank Test.—As the acetic anhydride and sodium acetate may contain impurities which affect the result it is necessary to make a blank test, using the same quantities of acetic anhydride and sodium acetate as in the analysis. After neutralizing the acetic acid, it is not necessary to add more than 5 c.c. of the $N/_1$ alkali (D) as that represents the excess of alkali usually left after saponification of the triacetin in the glycerol determination.

Determination of the Glycerol Value of the Acetylizable Impurities.—The total residue at 160° C. is dissolved in 1 or 2 c.c. of water, washed into a clean acetylizing flask 120 c.c. capacity and the water evaporated. Now add anhydrous sodium acetate and proceed as in the glycerol determination before described. Calculate the result to glycerol.

Analysis of Acetic Anhydride.—Into a weighed stoppered vessel, containing 10 to 20 c.c. of water, run about 2 c.c. of the anhydride, replace stopper and weigh; allow to stand, with occasional shaking, for several hours, till all anhydride is hydrolysed; then dilute to about 200 c.c., add phenolphthalein and titrate with $^{N}/_{1}$ NaOH. This gives the total acidity due to free acetic acid and acid formed from anhydride.

Into a stoppered weighing bottle containing a known weight of recently-distilled aniline (from 10 to 20 c.c.) measure about 2 c.c. of the sample, stopper, mix, allow to cool, and weigh. Wash contents into about 200 c.c. cold water, and titrate acidity as before. This yields the acidity due to the original, preformed, acetic acid plus one-half the acid due to anhydride (the other half having formed acetanilide); subtract the second result from the first (both calculated for 100 gm.) and double result, obtaining c.c. $^{N}/_{1}$ NaOH per 100 gm. sample. 1 c.c. $^{N}/_{1}$ NaOH equal 0·0510 gm. acetic anhydride. (See p. 96.)

BICHROMATE PROCESS.

Re-agents Required.—(A) **Pure Potassium Bichromate** powdered and dried in air free from dust or organic vapours, at 110° to 120° C. This is taken as the standard.

(B) **Dilute Bichromate Solution.**—7·4564 gm. of the above bichromate (A) are dissolved in distilled water, and the solution made up to one litre at 15·5° C.

(C) **Ferrous Ammonium Sulphate.**—Dissolve 3·7282 gm. of potassium bichromate (A) in 50 c.c. of water. Add 50 c.c. of 50 per cent. (by volume) sulphuric acid, and to the cold undiluted solution add from a weighing bottle a moderate excess of the ferrous ammonium sulphate, and titrate back with the dilute bichromate (B). Calculate the value of the ferrous salt in terms of bichromate.

(D) **Silver Carbonate.** This is prepared as required for each test from 140 c.c. of 0·5 per cent. silver sulphate solution by precipitation with about 4·9 c.c. $^{N}/_{1}$ sodium carbonate solution (a little less than the calculated quantity of $^{N}/_{1}$ sodium carbonate should be used; any excess of alkali carbonate prevents rapid settling). Settle, decant and wash once by decantation.

(E) **Subacetate of Lead.** Boil a pure 10 per cent. solution of lead acetate with an excess of litharge for one hour, keeping the volume constant, and filter while hot. Disregard any precipitate which subsequently forms. Preserve out of contact with carbon dioxide.

(F) **Potassium Ferricyanide.**—A very dilute solution containing about 0·1 per cent.

METHOD OF PROCEDURE: Weigh 20 gm. of the glycerine, dilute to 250 c.c. and take 25 c.c. Add the silver carbonate, allow to stand, with occasional agitation, for about 10 minutes, and add a slight excess (about

5 c.c. in most cases) of the basic lead acetate (E), allow to stand a few minutes, dilute with distilled water to 100 c.c. and then add 0·15 c.c. to compensate for the volume of the precipitate, mix thoroughly, filter through an air dry filter into a suitable narrow mouthed vessel rejecting the first 10 c.c., and return filtrate if not clear and bright. Test a portion of the filtrate with a little basic lead acetate, which should produce no further precipitate. (In the great majority of cases 5 c.c. is ample.) Occasionally a crude will be found requiring more, and in this case another aliquot of 25 c.c. of the dilute glycerine should be taken and purified with 6 c.c. of the basic acetate. Care must be taken to avoid a marked excess of basic acetate.

Measure off 25 c.c. of the clear filtrate into a glass flask or beaker (previously cleaned with potassium bichromate and sulphuric acid). Add 12 drops of sulphuric acid (1 : 4) to precipitate the small excess of lead as sulphate. Add 3·7282 gm. of the powdered potassium bichromate (A). Rinse down the bichromate with 25 c.c. of water and stand with occasional shaking until all the bichromate is dissolved (no reduction will take place).

Now add 50 c.c. of 50 per cent. sulphuric acid (by volume) and immerse the vessel in boiling water for two hours and keep protected from dust and organic vapours, such as alcohol, till the titration is completed. Add from a weighing bottle a slight excess of the ferrous ammonium sulphate (C) making spot tests on a porcelain plate with the potassium ferricyanide (F). Titrate back with the dilute bichromate. From the amount of bichromate reduced calculate the percentage of glycerol.

1 gm. glycerol = 7·4564 gm. bichromate.
1 „ bichromate = 0·13411 „ glycerol.

Notes. (1) It is important that the concentration of acid in the oxidation mixture and the time of oxidation should be strictly adhered to.

(2) Before the bichromate is added to the glycerine solution it is essential that the slight excess of lead be precipitated with sulphuric acid as stipulated in the process.

(3) For crudes practically free from chlorides the quantity of silver carbonate may be reduced to one-fifth, and the basic lead acetate to 0·5 c.c.

(4) It is sometimes advisable to add a little potassium sulphate to ensure a clear filtrate.

Instructions for Calculating Actual Glycerol Content.—(1) Determine the apparent percentage of glycerol in the sample by the acetin process as described. The result will include acetylizable impurities if any be present.

(2) Determine the total residue at 160° C.

(3) Determine the acetin value of the residue at (2) in terms of glycerol.

(4) Deduct the result found at (3) from the percentage obtained at (1) and report this corrected figure as glycerol. If volatile acetylizable impurities are present these are included in this figure.

Notes and Recommendations.—Experience has shown that in crude glycerine of good commercial quality, the sum of water, total residue at 160° C. and corrected acetin result comes to within 0·5 of 100. Further, in such crudes the bichromate result agrees with the uncorrected acetin result to within 1 per cent.

In the event of greater differences being found, impurities such as polyglycerols or trimethylene glycol are present. Trimethylene glycol is more volatile than glycerine; it can therefore be concentrated by fractional distillation. An approximation to the quantity can be obtained from the spread between the acetin and bichromate results of such distillates. Trimethylene glycol showing by the former method 80·69 per cent., and by the latter 138·3 per cent. expressed as glycerol.

If the non-volatile organic residue at 160° C. in the case of a soap lye crude be over 2·5 per cent., i.e. when not corrected for carbon dioxide in the ash, then the residue shall be examined by the acetin method, and any excess of glycerol found over 0·5 per cent. shall be deducted from the acetin figure.

In the case of saponification, distillation and similar glycerines, the limit of organic residue which should be passed without further examination shall be fixed at 1 per cent. In the event of the sample containing more than 1 per cent., the organic residue must be acetylated, and any glycerol found (after making the deduction of 0·5 per cent.) shall be deducted from the percentage of glycerol found by the acetin test.

In valuing crude glycerine for certain purposes it is necessary to ascertain the approximate proportion of arsenic, sulphides, sulphites, and thiosulphates.

(End of International Methods.)

Determination of Glycerol in Oils and Fats, etc.—20 gm. of the fat or oil are saponified with alcoholic potash or soda as in determining the Reichert value (see p. 393). The soap is dissolved in a considerable volume of water, and decomposed with dilute sulphuric acid, the precipitated fatty acids are filtered off, an excess of barium carbonate is added to the filtrate, which is then evaporated on the water-bath until most of the water has been driven off. The residue is then extracted with a mixture of ether (1) and 95 per cent. alcohol (3), the bulk of the ether-alcohol volatilized carefully on the water-bath and the residue dried in a dessicator (preferably in a vacuum) and weighed. 1 to 1·5 gm. of the crude glycerin thus obtained is then taken for the determination of glycerol present by the acetin or by an oxidation method.

Glycerol in pharmaceutical preparations, such as "glycerin of tannic acid" may be determined by first adding a solution of basic lead acetate, removing the excess of lead from the filtered solution by means of H_2S, and evaporating the filtrate till free from H_2S. Excessive evaporation must be avoided or glycerol will be lost. The glycerol present is then determined by the acetin method.

INDIGO.

(Indigotin $C_6H_{10}N_2O_2$.)

THE determination of indigotin in commercial indigo is a matter of great importance to the dyeing trade and many methods have been described for its accomplishment. C. Rawson[1] was one of the earliest workers in this field, and, briefly, his method of valuation consisted in sulphonating the indigo by heating with pure sulphuric acid at 70° to 80° for an hour, diluting, purifying the solution of indigotin-disulphonic acid obtained by addition of barium chloride solution, and titrating a known volume of the clear liquid, largely diluted with water, with approximately $^N/_{50}$ permanganate until all the blue colour disappears. Rawson found, as the result of his determinations that

---

[1] *Journ. Soc. Dyers and Colourists*, 1885, **1**, 74, and *J. S. C. I.*, 1889, **18**, 251.

1 part of permanganate = 2·373 indigotin.

The above process has been critically examined by Bergtheil and Briggs[1] with the following results:—

Three samples of pure indigotin were each found to contain 10·59 per cent. nitrogen[2] (= 99·1 per cent. indigotin), 0·3 gm. of each sample was sulphonated and the solution made up to 500 c.c. Of this latter solution 25 c.c. required 10·05, 10·00 and 10·05 c.c. respectively of $^N/_{49\cdot45}$ permanganate.

Using Rawson's factor these contain 99·39, 98·9, and 99·39 per cent. of indigotin. Similarly, 0·5 gm. being taken instead of 0·3 gm., 16·7 c.c. of permanganate were required and 99·1 per cent. of indigotin found. In all cases the factor used was

1 c.c. $^N/_{50}$ permanganate = 0·0015 gm. indigotin.

It should be noted that in all the above experiments no barium chloride or other purifying agent was used, since no impurities were present. The authors remark that "The reaction is admittedly a progressive one, and it is therefore necessary to conduct the titration rapidly and to take the disappearance of the blue colour as an indication of its completion". With respect to the effect of adding barium chloride to bring about the removal of suspended impurities from solutions of commercial indigos, the authors record experiments showing that precipitation by barium chloride involves a loss of indigotin, which is carried down with the barium sulphate. They found, however, that a precipitate of barium sulphate, freshly formed out of contact with the solution of indigotin-disulphonic acid, and added to the latter as such, did not cause any precipitation of indigotin to take place, while by thoroughly shaking the barium sulphate in the solution efficient purification is secured. They finally recommend the following method of procedure as combining the most rapid working with the highest accuracy:

0·5 gm. of finely powdered indigo is placed in a small, narrow-necked stoppered bottle, and mixed with a few Bohemian garnets. 20 c.c. of pure concentrated sulphuric acid are added and the bottle, with its stopper removed, placed in a shallow water-bath containing just enough water to cover the depth of acid in the bottle. The bath is now brought to the boil, and when briskly boiling the stopper is replaced in the bottle, which is shaken periodically for 15 minutes. At the end of this time the bottle is removed from the water-bath, and allowed to remain in cold water with its stopper removed until the contents are cool. These are then transferred to a 500 c.c. flask in which 10 c.c. of a 20 per cent. solution of barium chloride and sufficient sulphuric acid to precipitate all the barium has previously been placed, and the whole made up to a volume, well shaken, and set aside for 1 hour for the precipitate to settle. An aliquot part of the supernatant liquid is then titrated with approximately $^{N}/_{50}$ permanganate, and the result calculated on the basis that

---

[1] *J. S. C. I.*, 1906, **25**, 729.

[2] Pure indigotin contains 10·68 per cent. N and N × 9·357 = indigotin.

1 c.c. $^{N}/_{50}$ permanganate = 0·0015 gm. indigotin.

The authors also examined another method, due to Grossmann,[1] of removing the suspended impurities from the diluted solution of indigotin-disulphonic acid. This consists in neutralizing the solution with pure calcium carbonate, the calcium sulphate which is precipitated carrying down all suspended impurities. They found that with pure indigotin and high grade indigos low results were obtained, but that with indigos of average commercial purity the loss of indigotin so occasioned is very small indeed.

W. P. Bloxam,[2] who was employed in India (1902-1904) in research work on plant indigo, and afterwards continued the work in the Cloth-Workers' Laboratory of the University of Leeds, after carefully examining all the methods that had previously been proposed for the analysis of indigo, devised the following method, which is known as

BLOXAM'S POTASSIUM TETRASULPHONATE METHOD.—**Preparation of Pure Indigotin.** This is necessary in order to serve as a standard. Dry and finely powdered crude indigo is placed in a long-necked Jena flask connected with a water pump, a catch-bottle being inserted between the flask and the pump. The pressure is reduced as far as possible, and the flask is lowered into a bath of heated fusible metal. A square of asbestos cardboard is so arranged that the portion of the flask between the level of the fusible metal and the cardboard is raised to such a temperature that only indigotin vapour is there present, and that this zone of the flask remains quite clear at the end of the operation, the sublimate being deposited in the upper portion of the flask above the asbestos cardboard. Sublimation commences at 300° and is finally effected between 370° and 390° C. A beautifully crystalline product is thus obtained, which, after washing with boiling acetic acid, followed by boiling alcohol, is usually chemically pure.

Solutions Required.—(*a*) *The Precipitant.* Potassium acetate solution, 450 gm. per litre (filtered). [Sodium acetate does not answer, since the sodium tetrasulphonate is obtained in the non-crystalline state.]

(*b*) *The Isotonic.*—Made by adding 5 c.c. of glacial acetic acid to 200 c.c. of (*a*) and then making up to 600 with water.

METHOD OF PROCEDURE: First of all a standard solution of indigotin is prepared as follows:—

1 gm. of pure indigotin, previously dried at 110° and cooled in a desiccator, is weighed out into a 30 c.c. spouted beaker, to it is added 2 to 3 gm. of purified sand, and 5 c.c. of fuming sulphuric acid (20 per cent. SO_3) are run in from a burette. After well stirring with a short glass rod, the beaker is covered with a watch-glass and heated in the water-oven

---

[1] *J. S. C. I.*, 1905, **24**, 308.

[2] W. P. Bloxam, *J. C. S.*, 1905, **87**, 974, and *J. S. C. I.*, 1906, **25**, 735.

for half an hour (crude indigos are sulphonated with 25 per cent. fuming acid for 35 minutes), stirring being repeated at intervals.

After cooling, the sulphonic acid is poured into a 500 c.c. measuring flask containing some water, and the beaker, stirring rod, and sand are repeatedly washed with water. Finally the cold solution is made up to the mark with water when

500 c.c. = 1 gm. indigotin + 5 c.c. fuming sulphuric acid.

100 c.c. of the above solution are now pipetted into a fairly large conical spouted beaker, and 100 c.c. of the precipitant are added from a burette provided with a constant supply of the precipitant.

(*a*) Precipitation is observed when the solutions are well agitated in the conical beaker. The beaker and its contents are now well warmed until complete solution is attained. Cooling is now effected in a stream of running water, and when the contents of the beaker are water-cold the beaker is transferred to a vessel containing ice and water. Here the beaker is left for 1 hour, during which time the tetrasulphonate settles out as a fine-grained crystalline precipitate, which will filter well. Meanwhile the isotonic solution is placed in a spouted conical beaker and cooled by immersion in ice and water. The whole is filtered by suction through a Gooch crucible, the paper in which is set by a small quantity of the cooled isotonic solution. The tetrasulphonate precipitate is washed with the ice-cold isotonic solution.

With good manipulation the operation is complete in a few minutes. In the case of pure indigotin a carefully performed analysis will yield a filtrate almost colourless. The very pale blue colour can be imitated by diluting a solution of tetrasulphonate of known indigotin value. In this way the indigotin strength of the filtrate, when the process is working well, is estimated at 1 part of indigotin in 3,000,000 of water, a loss which is entirely negligible.

The Gooch crucible is now placed in a funnel which rests in the neck of a 200 c.c. measuring flask. With the aid of hot water this is washed free from blue, and any precipitate which adheres to the walls of the conical beaker is dissolved and added to the main fluid, which on cooling is made up to the mark. Portions of this solution are used for the determination of indigotin :—

(*a*) **By means of Standard Potassium Permanganate** (**1 in 1000**).—20 c.c. of the solution are transferred to a shallow porcelain dish and 80 c.c. of distilled water and 0·5 c.c. of pure concentrated sulphuric acid are added. This solution, which is not of a greater concentration than 1 in 5000, is titrated with the permanganate solution until the addition of a drop no longer produces a cloud in the pure yellow liquid. Indigotin (100 per cent.) would require in these circumstances 9·0 c.c. of permanganate, and percentages are calculated from this standard.

(*b*) **By means of Titanium Trichloride.**—In this case 25 c.c. of the solution of potassium tetrasulphonate is used for each determination. This volume of solution is delivered into a 300 c.c. conical Jena flask and to it is added 1·5 c.c. of a 20 per cent. solution of normal sodium tartrate. The liquid is then heated to boiling and titrated whilst hot with a current of carbon dioxide passing through the flask.

Each of the above methods determines indirubin simultaneously with indigotin.

NOTE.- For preparation of standard titanium trichloride see p. 240.

Determination of Indigo-Red in Indigo (W. P. Bloxam and A. G. Perkin).[1]

The dyestuff, mixed with purified sand, is introduced into a glass tube (about 25 × 90 mm.) closed at one end with calico, which is placed in a Soxhlet tube and the material extracted with pyridine. The pyridine extract is evaporated finally with the addition of hot water, and the precipitate, which consists of indirubin and a little indigotin together with impurities, is collected on asbestos, washed with dilute hydrochloric acid to remove mineral matter, with 1 per cent. alkali to dissolve indigo-brown, and finally with 1 per cent. acetic acid solution. The crystalline residue is dried, sulphonated, and the solution of the mixed sulphonic acids analysed by means of the Duboscq colorimeter.

The residual mixture of sand and crude indigotin is washed in the Soxhlet apparatus with hot 10 per cent. sulphuric acid, which removes indigo-gluten and some mineral matter, and with water until free from acid; the residue is then dried and sulphonated in the ordinary manner, the product dissolved in water, the solution filtered, and titrated with permanganate, or titanium trichloride. The accuracy of the process has been determined by an examination of mixtures of pure indigotin and indirubin, and the reliability of the colorimetric work, in respect of the amount of colouring matter present, by means of titanium chloride.

OILS, FATS, AND WAXES.

UNDER the terms oils, fats, and waxes (liquid and solid) are comprised all those naturally-formed substances, derived from both the vegetable and the animal kingdoms, which consist mostly of glyceryl or other esters of the higher members of the several series of fatty or aliphatic acids, with which in some cases notable amounts of the free fatty acids and of the free alcohols themselves are admixed. The term wax is also used to designate certain solid hydrocarbons, the mineral waxes (e.g., paraffin wax, ozokerite).

In the examination of the above as to their identity and for the detection of adulteration, valuable aid is lent by physical methods of examination, such as specific gravity, refractive index, rotatory power, etc., for an account of which other works must be consulted. The chemical methods of examination are based on the determination of "values," which furnish a measure of the quantity of the acids, alcohols, etc., present in the sample examined, without, however, fixing their absolute quantity. In order to secure comparable results, it is absolutely essential to adhere strictly to the minutest details as to the preparation of reagents and manipulation of experiment prescribed for each determination. The most important "values" are the following:—

---

[1] *J. C. S.*, 1910, **26**, 168.

(1) Acid value.

(2) Saponification or Köttstorfer value.

(3) Reichert (Reichert-Meissl or Reichert-Wollny) value.

(4) Acetyl value.

(5) (Bromine or) Iodine value.

In addition to the above, the percentage of insoluble fatty acids is sometimes referred to as the "Hehner value". It usually ranges from about 95·5 to 96 per cent. in the case of fats containing only minute quantities of soluble fatty acids. It should be noted, however, that the insoluble fatty acids obtained from oils and fats after saponification contain varying amounts of unsaponifiable matter. Hence the term "Hehner value" comprises insoluble fatty acids + unsaponifiable matter. The "Polenske value" will be referred to in connection with the Reichert value.

The Acid Value.—This is determined by the number of milligrams of potassium hydrate (KOH) required to saturate the free fatty acids in 1 gm. of oil, fat, or wax.

The standard alkali used in this process may be of $^{N}/_{2}$, $^{N}/_{5}$, or $^{N}/_{10}$ strength, according to the nature and amount of fat, and may be either in aqueous or alcoholic solution, and the indicator is preferably phenolphthalein. The sample may be dissolved in pure alcohol, methyl alcohol, purified methylated spirit, or a mixture of alcohol and ether; but whatever solvent is used it should be tested for acidity, and if any is present it is best neutralized exactly with $^{N}/_{10}$ alkali.

Liquid fats, say about 10 gm., are weighed into a flask, and about 50 c.c. of the neutral solvent, with a few drops of indicator, added. The titration is then made with constant shaking, the alkali solution being run in slowly.

The first appearance of a pink colour is accepted as the end; otherwise by standing a little time the colour may disappear, owing to saponification of neutral esters. Solid fats or waxes should be heated on a water-bath until the solvent boils, then at once titrated.

In some substances alcohol alone will not give a clear solution (which does not really matter), but if a clear solution is desired a mixture of ether and alcohol may be used and the titration made with alcoholic alkali. The number of c.c. of standard potash used taken in milligrams of KOH will give the calculation for acid value.

If F gm. of fat or oil require N c.c. of $^{N}/_{10}$ alkali solution, then

$$\text{Acid value} = \frac{N \times 5{\cdot}61}{F}.$$

In order to express the acidity in percentages of oleic acid, the formula required is

$$\text{Oleic acid per cent.} = \frac{N \times 2{\cdot}82}{F}.$$

In the case of fats obtained from the kernels of the coconut group, such as coconut oil, palm kernel oil, tucum, babassu, etc., the acidity is calculated as lauric acid by the following formula:—

$$\text{Lauric acid per cent.} = \frac{2\text{N}}{\text{F}}.$$

EXAMPLE.—3·254 gm. of tallow treated as above required 3·5 c.c. of $^{\text{N}}/_{10}$ KOH or 3·5 × 5·61 mgm. KOH. Hence acid value $= \frac{3·5 \times 5·61}{3·254} = 6·03$.

The percentage of free fatty acids (expressed as oleic acid) is obtained by multiplying the acid value by 0·503.

Saponification or Kottstorfer Value.—This indicates the number of milligrams of potassium hydroxide required for the complete saponification of 1 gm. of a fat or wax. It expresses the amount of potassium hydroxide, in tenths per cent., required to neutralize the total fatty acids in 1 gm. of a fat or wax.

The solutions required are:—

Standard hydrochloric acid.—Semi-normal strength, i.e. 18·234 gm. per litre.

Standard solution of caustic potash in alcohol.—This should contain about 30 gm. of KOH per litre. Methylated spirit[1] in which caustic potash has been dissolved and allowed to stand for several days, and then distilled, may be used in place of pure alcohol. In any case the strength should not be less than 90 per cent., and the solution should be made from alcohol which will not give a yellow colour after being boiled with very strong solution of caustic potash and left standing for half an hour. As the solution changes in strength, it is not possible to rely upon its being semi-normal, but it should be roughly adjusted at about that strength with absolutely accurate hydrochloric acid, and *a blank experiment made side by side with each titration of fat.* It is best kept in the dark. The excess of potash used in the fat titration is thus expressed in terms of $^{\text{N}}/_{2}$ acid, and to arrive at the percentage of potash, each c.c. is multiplied by 0·02805. The "saponification equivalent" of the fat or oil is found by dividing the weight of the sample in milligrams by the number of c.c. of normal (not $^{\text{N}}/_{2}$) acid corresponding to the alkali neutralized by the oil. If the percentage of potash is known, the saponification equivalent may be found by dividing this percentage into 5611, or if NaHO is the alkali used, into 4001.

METHOD OF PROCEDURE: About 2 gm. of the clear filtered fat are weighed into a dry 200 c.c. flask of resistance glass, 25 c.c. of neutral alcohol, then 25 c.c. of standard potash solution added by means of a pipette. At the same time another 25 c.c. of the same alcohol and 25 c.c. of the alcoholic potash solution are run into a similar flask. The flasks are connected to reflux condensers, and heated preferably in a water-bath, so that the alcohol boils briskly for 30 minutes. The fat-containing flask should be shaken with a rotary movement from time to time during the period. 1 c.c. of phenolphthalein solution is then added to each flask, and the contents titrated while hot with $^{\text{N}}/_{2}$ acid.

---

[1] "Industrial" methylated spirit is the most suitable for this purpose, as it remains clear on dilution with distilled water.

Results are calculated as shown in the following example:—

Example.—1·532 gm. of olive oil were saponified with 25 c.c. of alcoholic potash, and 12·0 c.c. of $^N/_2$ hydrochloric acid were required to titrate back. Another 25 c.c. of alcoholic potash measured out at the same time required for the blank test 22·5 c.c. of the standard acid.

Hence, the amount of potash used for saponification was

$(22·5 - 12·0) \times 0·02805$ gm. = 294·5 mgm. KOH for 1·532 gm fat,

or for 1 gm. of fat

$$\frac{294·5}{1·532} = 192·2 \text{ mgm. KOH.}$$

The method of calculation adopted by Kottstorfer is to ascertain the number of milligrams of KHO required to saturate the acids contained in 1 gm. of fat, or, in other words, parts per 1000. He found that, operating in this way, pure butters required from 221·5 to 232·4 mgm. of KHO for 1 gm., whereas the fats usually mixed with butter, such as beef, mutton, and pork fat, required a maximum of 197 mgm. for 1 gm., and other oils and fats much less.

Practically this means that the amount of KHO required for genuine butters ranges from 23·24 to 22·15 per cent., the latter being the inferior limit. If caustic soda is used instead of potash, other numbers must, of course, be used.

The following list shows the parts of KHO required per 1000 of fat; the first four being calculated from their known equivalents, the rest obtained experimentally by Köttstorfer, Allen, Stoddart, or Archbutt:—

Tripalmitin	208·8	Niger oil	190·2
Tristearin	189·1	Linseed	192 to 195
Triolein	190·4	Cotton seed	193 ,, 195
Tributyrin	557·3	Whale	188 ,, 194
Coconut oil	246 to 260	Seal	189 ,, 196
Dripping	197·0	Rape (colza)	170 ,, 179
Lard	195·4	Cod liver oil	171 ,, 189
Horse fat	195 to 197	Castor	183 ,, 186
Lard oil	191 ,, 196	Sperm	123 ,, 147
Olive oil	185 ,, 196	Shark liver	161

Acid Value and Saponification Value (Combination Method).—These determinations may be made consecutively on the same weighed amount or sample as follows:—

About 4 gm. of the clear filtered fat or oil are weighed into a saponification flask and 25 c.c. of hot alcohol containing 1 c.c. of phenolphthalein solution, and previously neutralized, are added. Standardized alcoholic alkali solution is then run into the solution from a burette until the liquid becomes pink, warming if necessary. The number of c.c. required by the free fatty acids is noted and the addition of alcoholic alkali continued till 50 c.c. in all have been added. The process is then concluded as described above. A blank test is made with 50 c.c. of the alcoholic alkali delivered from the same burette, similar quantities of all the reagents being likewise used.

The Ester Value.—This indicates the number of milligrams of KOH required for the saponification of the neutral esters in 1 gm. of a fat or wax.

Where the fat contains no free fatty acids the ester value is the same as the previously mentioned saponification value, but as many fats or waxes do contain small quantities of free fatty acids the saponification value includes both, and therefore the ester value is the difference between the saponification and the acid value.

The Reichert (Reichert-Meissl, Reichert-Wollny) Value.—This indicates the number of c.c. of ${}^{N}/_{10}$ KOH required for the neutralization of that portion of the soluble volatile fatty acids which is obtained from 2·5 (or 5) gm. of a fat or wax by the Reichert distillation process.

Reichert originally used 2·5 gm. of substance, but Meissl suggested that 5 gm. would be a more convenient quantity, and this is the amount now generally used. Wollny, in his modification of the Reichert process, also uses 5 gm. of substance. It is important to note that this process and its modifications do not yield absolute values; they merely give a measure of the total volatile acids present in an oil, fat, or wax. For purposes of comparison, especially in the examination of butter fat, the relative numbers thus obtained are of great value. The numbers given by the Meissl and Wollny modifications are not necessarily twice the Reichert value. In the case of butter fat, however, it is quite admissible to work with 2·5 gm. and to multiply the result by 2·2 in order to obtain numbers comparable with those found by the Reichert-Meissl or the Reichert-Wollny process. On the other hand the quantity of 5 gm. must be rigorously adhered to in the case of coconut oil and palm kernel oil.

The description of the process as used for butter will practically apply to other fatty matters.

BUTTER.

The Reichert or Reichert-Meissl Method.—This process consists in saponifying the fat to be examined by an alkali, separating the fatty acids by neutralizing the alkali, and distilling off the volatile acids (chiefly butyric and caproic) for titration with standard acid. In this and Köttstorfer's method, where also alcoholic solution of caustic alkali is used, it is essential to avoid absorption of CO_2 by long exposure.

The necessary solutions are:—

1. Standard barium or potassium hydrate. ${}^{N}/_{10}$ strength is most convenient, but any solution approximating to that strength may be used, and a factor found to convert it to that strength in calculating the results of titration. It must be carefully preserved from CO_2 by any of the usual arrangements, and where a constant series of titrations are carried on, it is best to have a store-bottle and burette fitted, as shown p. 13, fig. 12.

2. Phenolphthalein indicator, see p. 37.

3. Alcohol of about 90 per cent. strength, and free from acid or aldehyde.

4. Solution of caustic soda. Made by dissolving 100 gm. of good sodium hydrate in 100 c.c. of distilled water which has been recently well boiled and cooled; this solution will not be contaminated with CO_2 to any extent, since any Na_2CO_3 which might be formed is quite insoluble in the strong solution; it must be allowed to stand until quite clear, then poured off and well preserved. Or better than this, about 2 gm. of solid stick potash or soda may be added with 50 c.c. of 70 per cent. alcohol to 5 gm. of butter when commencing saponification.

5. Sulphuric acid for separating the fatty acids is made by diluting 25 c.c. of strongest H_2SO_4 to a litre with water.

6. The apparatus for digestion and distillation are shown in fig. 50, the same Erlenmeyer flask being used for the digestion and for the distillation. The distilled liquid drops into a small funnel containing a small porous filter for separating any scum which may pass over with the distillate; the receiver holding the funnel is marked at 50 c.c. and 100 c.c., so as to be available for either 2·5 gm. or 5 gm. of butter fat.

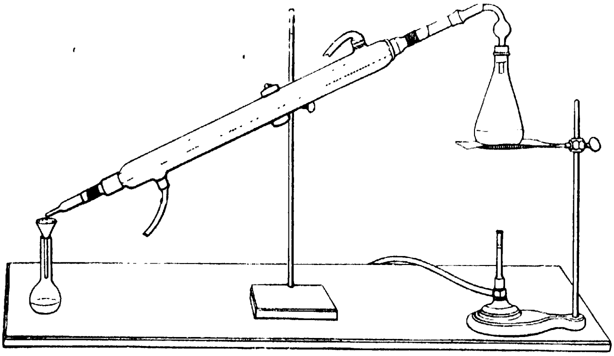

Fig. 50.

The following method of manipulation as drawn up by the Association of Official Agricultural Chemists, U.S.A., is recommended as being all that is required to ensure accuracy, and applies to the treatment fo approximately 5 gm. of fat for each operation. Many operators prefer to take about half that quantity, which saves time, and need not be any the less accurate.

PROCESS: WEIGHING THE FAT: The butter or fat to be examined should be melted and kept in a dry, warm place at about 60° C. for 2 or 3 hours until the moisture and curd have entirely settled out. The clean supernatant fat is poured off and filtered through a dry filter-paper in a jacketed filter containing boiling water, to remove all foreign matter and any traces of moisture. Should the filtered fat in a fused state not be perfectly clear the treatment above mentioned must be repeated.

The saponification flasks are prepared by having them thoroughly washed with water, alcohol, and ether, wiped perfectly dry on the outside, and heated for one hour to 100° C. The flasks should then be placed in a tray by the side of the balance and covered with a silk handkerchief until they are perfectly cool. They must not be wiped with a silk handkerchief within 15 or 20 minutes of the time they are weighed. The weight of each flask is determined accurately, using a flask for a counterbalance or not, as may be convenient. The weight of the flasks having been accurately determined they are charged with the melted fat in the following way:—

A pipette with a long stem marked to deliver 5·75 c.c. is warmed to a temperature of about 50° C. The fat having been poured back and forth once or twice into a dry beaker in order to thoroughly mix it, it is taken up in the pipette, the nozzle of the pipette carried to near the bottom of the flask, it having been previously wiped to remove any adhering fat. The 5·75 c.c. of fat are allowed to flow into the flask and the pipette is removed. After the flasks have been charged in this way they should be re-covered with the silk handkerchief and allowed to stand 15 or 20 minutes, when they are again weighed to ascertain the exact amount of fat.

THE SAPONIFICATION: 10 c.c. of 90 per cent. alcohol are added to the fat in the flask, 2 c.c. of the concentrated soda solution or 2 gm. of solid alkali are added, a soft cork stopper inserted in the flask and tied down with a piece of twine. The saponification is then completed by placing the flasks upon the water or steam bath. The flasks during the saponification, which should last for 1 hour, should be gently rotated from time to time, being careful not to project the soap for any distance up the sides of the flask. At the end of an hour the flasks, after having been cooled to near the room temperature, are opened. If solid alkali is used instead of aqueous solution, alcohol of 75 or 80 per cent. in larger quantity may be used.

REMOVAL OF THE ALCOHOL: The stoppers having been laid loosely in the mouth of the flasks, the alcohol is removed by dipping the flasks into a steam bath. The steam should cover the whole of the flask except the neck. After the alcohol is nearly removed, frothing may be noticed in the soap, and to avoid any loss from this cause, or any creeping of the soap up the sides of the flask, it should be taken from the bath and shaken to and fro until the frothing disappears. The last traces of alcohol vapour may be removed from the flask by waving it briskly, mouth down, to and fro. Complete removal of the alcohol with the precautions above noted should take about 45 minutes.

DISSOLVING THE SOAP: After the removal of the alcohol the soap should be dissolved by adding 100 c.c. of recently boiled distilled water, and warmed on the steam bath with occasional shaking until the soap is completely dissolved.

SETTING FREE THE FATTY ACIDS: When the soap solution has cooled to about 60° or 70° C., the fatty acids are separated by adding 40 c.c. of the dilute sulphuric acid mentioned above.

MELTING THE FATTY ACIDS: The flasks should now be re-stoppered as in the first instance, and the fatty acids melted by replacing the flasks on the steam bath. According to the nature of the fat examined the time required for the fusion of the fatty acids may vary from a few minutes to hours.

THE DISTILLATION: After the fatty acids are completely melted, which can be determined by their forming a transparent oily layer on the surface of the water, the flasks are cooled to room temperature and a few pieces of pumice stone added. The pumice stone is prepared by throwing it, at white heat, into distilled water, and keeping it under water until used. The flask is now connected with the condenser, slowly heated with a naked flame until ebullition begins, and then the distillation continued by regulating the flame in such a way as to collect 100 c.c. of the distillate in as nearly as possible 30 minutes.

Some operators distil 110 c.c. from 5 gm. of butter into an ordinary measuring flask, then filter and use 100 c.c. for titration, the number of **c.c.** of alkali used is multiplied by 1·1 which gives the Reichert-Meissl **value.**

The above methods of preparation are somewhat tedious, but experienced operators will find methods of working so as to occupy less time without loss of accuracy.

TITRATION OF THE VOLATILE ACIDS: The 100 c.c. of the filtered distillate are poured into a beaker holding from 200 to 250 c.c., 0·5 c.c. of phenolphthalein solution added, and decinormal barium or potassium hydrate run in until a red colour is produced. The contents of the beaker are then returned to the measuring flask to remove any acid remaining therein, poured again into the beaker, and the titration continued until the red colour produced remains apparently unchanged for 2 or 3 minutes.

Where the greatest accuracy is required it is best to carry out side by side a blank experiment with the same amounts of alcohol, alkali, etc.

It must be borne in mind that this method yields only a portion of the volatile fatty acids, but the experience of the author and a host of other very competent operators clearly shows that the distillate from 5 gm. of genuine normal butter fat produced in districts of medium temperature, when carried out as described, should require not less than 24 c.c. of $^{N}/_{10}$ alkali to neutralise the volatile acids present. It is true that butters known to be genuine have occasionally been found to give lower figures from some unexplained causes, one of which seems to be due to milk taken from cows towards the end of their period of lactation. The figure may also rise to 32 or 33 c.c. of alkali. This is often the case with butters produced in warmer climates than Great Britain. The general average for butters taken from the mixed milk of a number of cows will be between 27 and 28 c.c., whereas margarine (except when consisting largely of coconut oil) will rarely require more than 0·5 c.c., beef fat and lard about the same, while coconut oil, which gives the highest figures, requires about 7 c.c.

It may, therefore, be concluded that any sample of butter fat which requires less than 24 c.c. of $^{N}/_{10}$ alkali must be looked upon with suspicion.

The minimum value recommended in Great Britain, France, and Germany, is 24; Sweden, 23; and Italy, 20.

A Joint Committee of the Principal of the Government Laboratory and the Society of Public Analysts, adopted in 1900[1] the Reichert-Wollny method as the official method for determining the percentage of butter-fat in margarine, the object in view being to avoid discrepancies which might arise through the employment of different methods by individual analysts. The following is the official description of the method:—

The Reichert-Wollny method for determination of volatile fatty acids in Margarine and Butter.—"Five gm. of the liquid fat are introduced into a 300 c.c. flask, of the form seen in the figure (length of neck 7 to 8 cm., width of neck 2 cm.). Two c.c. of a solution of caustic soda (98 per cent.) in an equal weight of water- preserved from the action of atmospheric carbonic acid and 10 c.c. of alcohol (about 92 per cent.) are added, and the mixture is heated under a reflux condenser, connected with the flask by a T-piece, for 15 minutes in a bath containing boiling water. The alcohol is distilled off by heating the flask on the water-bath for about half an hour, or until the soap is dry. 100 c.c. of hot water, which have been kept boiling for at least 10 minutes, are added, and the flask heated until the soap is dissolved. 40 c.c. of normal sulphuric acid and three or four fragments of pumice or broken pipe-stems are added, and the flask is at once connected with a condenser by means of a glass tube 7 mm. wide and 15 cm. from the top of the cork to the bend. At a distance of 5 cm. above the cork is a bulb 5 cm. in diameter. The flask is supported on a circular piece of asbestos 12 cm. in diameter, having a hole in the centre 5 cm. in diameter, and is first heated by a very small flame, to fuse the

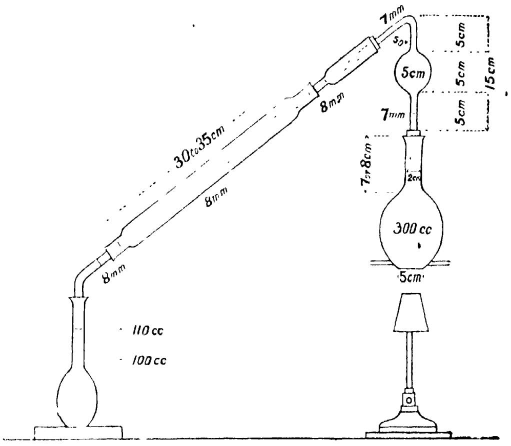

FIG. 51.

---

[1] See *Analyst*, 1900, **25**, 309.

insoluble fatty acids, but the heat must not be sufficient to cause the liquid to boil. The heat is increased, and when fusion is complete 110 c.c. are distilled off into a graduated flask, the distillation lasting about 30 minutes (say from 28 to 32 minutes), the distillate is shaken, 100 c.c. filtered off, transferred to a beaker, 0·5 c.c. of phenolphthalein solution (1 gm. in 100 c.c. alcohol) added, and the filtrate titrated with decinormal soda or baryta solution. Precisely the same procedure (with the same reagents), omitting the fat, should be followed, and the amount of decinormal alkali required to neutralize the distillate ascertained. This should not exceed 0·3 c.c. The volume of decinormal solution of alkali used, less the figure obtained by blank experiment, is multiplied by 1·1. The number so obtained is the "Reichert-Wollny Number".

NOTES ON THE METHOD: The sample is melted and filtered from curd and water through a dry filter. From the filtrate the 5 gm. of fat for the process are taken. The soda solution is filtered clear from carbonate formed in its preparation, and kept in a special bottle. The Soxhlet spherical condenser is a convenient one for the reflux distillation. This is fixed near the water-bath in which the saponification is to take place, and is connected with the flask by means of a T-piece and india-rubber tubes inclined at an angle of 45°. During the saponification the free limb of the T-piece is directed upwards, and its end closed by a short piece of india-rubber and glass rod. At the end of 15 minutes this limb is turned downwards, and the piece of glass rod, replaced by a tube carrying away the alcohol.

One hundred c.c. of hot distilled water are added, and the flask frequently shaken until the soap is dissolved. The Liebig is a convenient form of condenser. One containing a column of water 30 to 35 cm. in length gives sufficient condensing surface. After shaking the distillate about 5 c.c. are filtered through a dry paper into a 100 c.c. flask. This serves to wash out the flask. When the 100 c.c. are transferred to a beaker, the flask is not washed out, but the main quantity is neutralized with the standard solution of alkali and returned to the flask, then again transferred to the beaker and the titration completed.

The somewhat lengthy process of saponification in the above method may advantageously be replaced by the following, due to Leffmann & Beam:[1]

First, prepare a solution of 100 gm. caustic soda (98 to 99 per cent. powdered caustic answers well) in water and make up to 200 c.c. Put the solution in a bottle with a rubber stopper and allow to stand till quite clear. 25 c.c. of the clear solution are then pipetted into 125 c.c. of pure glycerin in a flask and well mixed. Next 5 gm. of the fat are placed in a 300 c.c. flask, 10 c.c. of the glycerol-soda added and the flask heated cautiously over a small Bunsen flame. Much foaming takes place, and the flask should be vigorously shaken. Complete saponification takes place in less than 5 minutes, the process being complete when the foaming has entirely ceased. The hot soap is then dissolved at once in 90 c.c. of water that has recently boiled, adding it drop by drop at first. Then 40 c.c. of dilute sulphuric acid are added, together with a few pieces of broken pipe-stem, and the distillation proceeded with as above. The usual blanks are 0·2 to 0·3 c.c. of $^{N}/_{10}$ alkali for the 110 c.c. of distillate.

---

[1] *Analyst*, 1891, **16**, 153; 1892, **17**, 65.

The glycerol-soda solution should be kept in a flask closed with a rubber stopper and measured by means of a rather wide glass tube marked to deliver 10 c.c.

Lewkowitsch[1] testifies to the fact that the values obtained by the above method are practically identical with that obtained by the Reichert-Wollny process.

The Water-insoluble Volatile Fatty Acids (Polenske).

This determination is best made by Polenske's method which is carried out as follows:—

Saponify 5 gm. of the filtered butter-fat by the Leffmann-Beam[2] process described above, taking care not to overheat the mixture of fat and glycerol-soda. Allow to cool below 100° C. before adding 90 c.c. of water, and dissolve the mass by warming on the water-bath to about 50° C. The solution must be clear and almost colourless; if of a brown colour, the test must be rejected. To the hot soap solution add 40 c.c. of the dilute sulphuric acid and 0·1 gm. of *finely powdered* pumice and attach immediately to the condenser. The apparatus used must agree in all details with the dimensions given in fig. 52. Regulate the heat so that in 19 to 20 minutes 110 c.c. are distilled over, and the flow of water through the condenser so that the distillate does not drop into the 110 c.c. flask at a higher temperature than 20° to 23° C. When 110 c.c. have distilled over, remove the burner and replace the flask by a 20 c.c. measuring cylinder. The 110 c.c. flask which must not be shaken, is immersed almost completely in water at 15° C. After 5 minutes' standing the neck is gently tapped so that the oily drops floating on the surface may adhere to the walls of the flask. After a further 10 minutes the consistence of the insoluble acids is noted, with a view to ascertaining whether they form a semi-solid mass or oily drops. The flask is then corked and its contents mixed by turning it upside down several times, avoiding, however, any violent shaking. 100 c.c. are then filtered through an 8 cm. dry filter and titrated with $^{N}/_{10}$ barium or potassium hydroxide, as in the Reichert-Wollny process. The insoluble volatile acids on the filter are washed

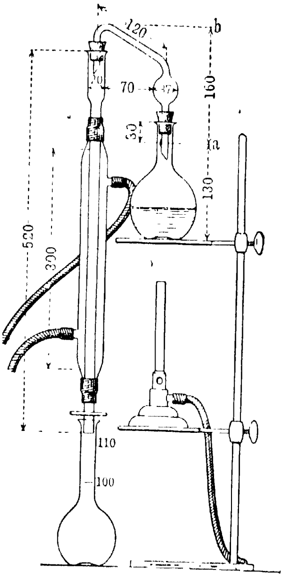

FIG. 52.

---

[1] *Oils, Fats, and Waxes*, 4th edition, Vol. I., 334.

[2] Alcohol being inadmissible in this process.

three times in succession with 15 c.c. of water that has previously been passed successively through the tube of the condenser the 20 c.c. measuring cylinder, and the 110 c.c. flask. These wash waters are rejected. The water-insoluble volatile acids are then collected by rinsing the condenser, cylinder, and flask three times in succession with 15 c.c. of neutralized 90 per cent. alcohol, and the alcoholic washings poured on to the filter—each being allowed to pass completely through before the next washing is added. The alcoholic filtrate is then titrated with $^{N}/_{10}$ alkali. The figure so obtained is called the Polenske value. For butter it varies from 1·5 to 3·0 c.c. and for coconut oil from 16·8 to 17·8 c.c. In order to obtain concordant results with this method, it is absolutely essential to follow the procedure given above in all its minutest details.

Lewkowitsch found that the Polenske values of genuine French and Finnish butters ranged from 2·24 to 4·1, and those of coconut oil from 15·5 to 20·45, while palm kernel oil gives values lying between 10 and 12. Several attempts have been made to determine the proportions of coconut oil in mixtures of coconut oil and butter fat by means of the Polenske number, but in view of the above range of values quantitative results should be received with great caution, especially with regard to alleged small additions of coconut oil to butter fat. Tatlock and Thomson[1] have also critically examined this process and express the opinion that "the possibility of the detection of even 10 per cent. of coconut oil in a butter by the Polenske method is very doubtful". But in the case of margarine "the Polenske number appears to be quite reliable within limits of say 5 per cent.". They obtained results within 3 per cent. of the truth, where there was 35 per cent. of coconut oil present. Margarine containing no coconut oil gave 0·4 Reichert-Wollny and 0·5 Polenske values.

The Acetyl Value.—This indicates the number of milligrams of KOH required for the neutralization of the acetic acid obtained on saponifying 1 gm. of an acetylated oil, fat, or wax. This treatment of fats was introduced by Benedikt, and a process by himself and Ulzer for acetylation and determination was arranged; but as the results were not consistent with modern ideas, Lewkowitsch[2] modified the method and proposed to determine the true acetyl value by actually titrating the amount of acetic acid assimilated by the hydroxylated acid in the form of acetyl C_2H_3O and given up on saponification as acetic acid to the standard alkali.

The method is as follows:

METHOD OF PROCEDURE: 10 gm., or any other convenient quantity, are boiled with twice the amount of acetic anhydride for 2 hours in a round-bottomed flask attached to an inverted condenser. The solution is then transferred to a beaker of about 1 litre capacity, mixed with 500 to 600 c.c. of boiling water and heated for half an hour, whilst a slow current of carbon dioxide is passed into the liquid through a finely drawn out tube reaching nearly to the bottom of the beaker; this is done to prevent bumping. The mixture is then allowed to separate into two layers, the water is siphoned off, and the oily layer again boiled out in the same manner three successive times. The last trace of acetic acid is thus removed—this being ascertained by testing with litmus paper. Prolonged washing beyond the required limit causes slight dissociation of the acetyl product. This would lead to too low an acetyl value. The acetylated product is then filtered through a dry filter-paper in a drying oven to remove water.

---

[1] *J. S. C. I.*, 1909, **28**, 69.

[2] *Ibid.*, 1897, **16**, 503.

This operation may be carried out quantitatively, and in that case the washing is best done with boiling water on a weighed filter. On weighing the acetylated oil or fat, an increase of weight would prove that assimilation of acetyl groups had taken place. This method may be found useful to ascertain preliminarily whether a notable amount of hydroxylated acids is present in the sample under examination.

About 5 gm. of the acetylated product are then saponified by means of alcoholic potash solution as in the well-known determination of the saponification value. If the "*disitllation process*" be adopted it is not necessary to work with an accurately measured quantity of standardized alcoholic potash. In case the "*filtration process*" be used, the alcoholic potash must be measured exactly. (It is, however, advisable to employ in either case a known volume of standard alkali, as one is then enabled to determine the saponification value of the acetylated oil or fat.) Next, the alcohol is evaporated and the soap dissolved in water. From this stage the determination is carried out either by (*a*) the "distillation process" or (*b*) the "filtration process".

(*a*) DISTILLATION PROCESS.—Add dilute sulphuric acid (1 : 10) more than is required to saturate the potash used, and distil the liquid as is usual in Reichert's distillation process. Since a large quantity of water must be distilled off, either a current of steam is blown through the suspended fatty acids or water is run into the distilling flask, from time to time, through a stoppered funnel fixed in the cork, or any other convenient device is adopted. It will be found quite sufficient to distil over 500 to 700 c.c., as the last 100 c.c. contain practically no acid. Then filter the distillates to remove any insoluble acids carried over by the steam, and titrate the filtrate with $^N/_{10}$ potash, phenolphthalein being the indicator. Multiply the number of c.c. by 5·61, and divide the product by the weight of substance taken. This gives the *acetyl value*.

(*b*) FILTRATION PROCESS.—Add to the soap solution a quantity of standardized sulphuric acid *exactly* corresponding to the amount of alcoholic potash employed, and warm gently, when the fatty acids will readily collect on the top as an oily layer. (If the saponification value has been determined, it is, of course, necessary to take into account the volume of acid used for titrating back the excess of potash.) Filter off the liberated fatty acids, wash with boiling water until the washings are no longer acid, and titrate the filtrate with $^N/_{10}$ potash, using phenolphthalein as indicator. The acetyl value is calculated in the manner shown above.

Both methods give identical results, but (*b*) will be found shorter and more convenient than (*a*).

The distilled water used in determining the value by either the distillation or the filtration process should be carefully freed from CO_2 by previous boiling, as otherwise serious errors may be made. Even the water used for generating steam in the distillation process should be brought to violent ebullition before the steam is passed into the distilling flask. This source of error may easily occur in the case of very hard water. Check experiments with pure acetic acid will readily guide the operator, if necessary. In order to facilitate the separation of the insoluble fatty acids in the filtration process, it will be found useful to add a slight excess of mineral acid. Of course this amount must be measured accurately, and deducted from the alkali required for determining the dissolved acids.

A full discussion as to the meaning of the acetyl value in fat analysis will be found in a lengthy paper by Lewkowitsch in *The Analyst*, 1899, **24**, 319.

The Bromine Value.—This indicates the percentage of bromine absorbed by a fat or wax. This determination was proposed by Cailletet in 1857; but the method of carrying it out is due to Mills[1] and his collaborators Snodgrass and Akitt. Mills found that it was of the utmost importance rigidly to exclude moisture when making the determination, since in the presence of water the value obtained was too high. He dissolved the sample of dried and filtered fat in carbon tetrachloride, added a standard solution of bromine in carbon tetrachloride in excess, and titrated back the excess with a standard solution of β-naphthol in carbon tetrachloride, when monobromonaphthol is formed. As, however, this determination has now been entirely superseded by the determination of Iodine value, the reader is referred, for further information, to the original papers on the subject already mentioned.[2]

The Iodine Value.—This indicates the amount of iodine chloride, expressed in per cent. of iodine, which a fat or wax is capable of absorbing. "This value is a measure of the proportion of unsaturated fatty acids, which, both in their free state and in combination with glycerol, have the property of assimilating halogens with formation of additive compounds" (Lewkowitsch). The method by which the determination was carried out was originated by Hubl,[3] who proved that from an alcoholic solution of iodine, in the presence of mercuric chloride, glycerides of the unsaturated fatty acids absorb iodine in a very regular, well-defined manner, when kept at the ordinary temperature, so that quantitative results can be obtained.

The following solutions are required for Hubl's process:—

1. Standard Iodine Solution.—This is made by dissolving respectively 25 gm. of iodine and 30 gm. of mercuric chloride, each as pure as possible, in separate portions of 500 c.c. each of 95 per cent. alcohol, then mixing the two liquids, and allowing to stand for 12 to 24 hours (preferably 3 days) before use. This solution must always be standardized at the time of using, and it is advisable not to mix a large quantity unless it is required for immediate use.

2. Solution of Sodium Thiosulphate.—Prepared by dissolving 25 gm. of the crystallized salt in a litre of water. It is standardized either by dissolving about 0·25 gm. of re-sublimed iodine, most accurately weighed, in potassium iodide solution (3 gm. dissolved in 5 c.c. of water), diluting to 25 c.c., and running in the thiosulphate solution from a burette till

---

[1] *J. S. C. I.*, 1883, **2**, 435; 1884, **3**, 366.

[2] A process for determining "the bromine addition" and "the bromine substitution" has been recorded by McIlhiney, *J. S. C. I.*, 1894, **13**, 688, also *J. A. C. S.*, 1899, 1084, and 1902, 1109.

[3] *Dingler's Polyt. Journal*, 1884, 281.

the solution has only a light yellow colour, then adding starch solution and continuing the addition of thiosulphate till the blue colour just disappears; or by the following method,[1] due to Volhard:—

Dissolve exactly 3·8633 gm. of pure potassium dichromate in a litre of water. Pipette 20 c.c. of the solution into a 200 c.c. stoppered bottle, add 25 c.c. of water, then 10 c.c. of 10 per cent. potassium iodide solution and 5 c.c. pure HCl, moisten the stopper with the KI solution, and allow to stand 5 minutes. In this way exactly 0·2 gm. of iodine is set free. Wash down the stopper with water, dilute to nearly 100 c.c., and titrate with thiosulphate solution.[2] The dichromate solution maintains its strength indefinitely, hence is always ready for standardizing a thiosulphate solution.

The following reactions take place:—

$$K_2Cr_2O_7 + 14HCl + 6KI = 8KCl + Cr_2Cl_6 + 7H_2O + 3I_2$$
$$3I_2 + 6Na_2S_2O_3 = 6NaI + 3Na_2S_4O_6.$$

Hence $K_2Cr_2O_7$ is equivalent to $3I_2$, or 294·2 gm. of the former to 761·52 of the latter, and 10 gm. of iodine are equivalent to 3·8633 gm. of dichromate. 1 c.c. of dichromate solution = 0·01 gm. iodine.

3. Chloroform or Carbon Tetrachloride.[3]—These should stand the following test for purity. Mix 10 c.c. with 10 c.c. of the iodine solution, allow to stand for 2 or 3 hours, and titrate. The volume of thiosulphate required should be the same as that required for 10 c.c. of the iodine solution alone.

4. Potassium Iodide Solution.—A 10 per cent. solution of the pure salt is used.

5. Starch Solution.—This should always be freshly made. About 0·5 gm. of starch is shaken with a little cold water in a test-tube, poured into about 50 c.c. of hot water in a larger tube, the liquid raised to the boiling point, then cooled for use. Or a 1 per cent. solution of soluble starch may be used.

Method of Procedure: From 0·15 to 0·2 gm. of a drying or fish oil 0·2 to 0·3 gm. of a semi-drying oil; 0·3 to 0·4 gm. of a non-drying oil; or 0·8 to 1 gm. of a solid fat is dissolved in 10 c.c. of chloroform or carbon tetrachloride in a well-stoppered, wide-mouthed bottle of about 300 to 400 c.c. capacity, and 25 c.c. of the iodine solution run in from a pipette, which should be drained for exactly 15 seconds. After not less than 4 hours' standing in a dark place the liquid should possess a dark brown tint; in any circumstances it is necessary to have a considerable excess of iodine (at least double the amount absorbed ought to be present) and the period of standing should be from 4 to 6 hours. At the end of that time some strong solution of potassium iodide should be added and about 150 c.c. of water (more iodide being added if the liquid does not remain clear), and standard thiosulphate run in at once from a burette, with constant shaking, till the liquid becomes yellow. Starch solution is then added and the titration finished in the usual way.

---

[1] Lewkowitsch, *Oils, Fats, and Waxes*, 4th Edition, Vol. I., p. 312.

[2] Or 0·2 gm. of pure dichromate may be weighed out and double the above amount of iodide and acid added. In this way 0·5177 gm. of iodine is set free.

[3] Lewkowitsch recommends carbon tetrachloride, since chloroform is liable to contain alcohol.

If after standing, say 2 hours, the solution has lost its deep brown colour, it is best to make a fresh experiment with either less fat or more iodine solution.

A blank experiment should in every case be made side by side with the sample, using the same proportions of chloroform and iodine solution.

Example.—To 0·4120 gm. of olive oil 10 c.c. of chloroform and 25 c.c. of Hübl's solution were added and allowed to stand for 4 hours. At the end of that time 18·9 c.c. of thiosulphate were required. The blank, consisting of 10 c.c. of chloroform and 25 c.c. of Hubl's solution, required 46·9 c.c. thiosulphate. Also

(i) 0·2704 gm. iodine required 21·3 c c. thiosulphate.
(ii) 0·2076 „ „ „ 16·35 c.c. „

$$\frac{\cdot 2704}{21\cdot 3} = \cdot 012695 \qquad \frac{\cdot 2076}{16\cdot 35} = \cdot 0127$$

Hence 1 c.c. thiosulphate = ·0127 gm. iodine.

$$\text{Iodine value} = \frac{(46\cdot 9 - 18\cdot 9) \times \cdot 0127 \times 100}{0\cdot 412}$$
$$= \frac{28 \times 1\cdot 27}{0\cdot 412}$$
$$= 86\cdot 3.$$

The values obtained by Hubl for various oils and fats are given in *J. S. C. I.*, 1884, **3**, 642.

The relative proportions in which two oils are mixed can be deduced from the iodine value of the mixture, thus

Let Ia be the mean iodine value of an oil a.
Ib „ „ „ b.
I the iodine value of the mixture.

Then

$$\text{percentage of oil } a = \frac{100\,(I - Ib)}{Ia - Ib}.$$

Example.—A mixture of cotton seed and olive oils gave the iodine value 91, hence

$$\text{cotton seed oil} = \frac{100(91 - 85)}{109 - 85} = 25 \text{ per cent.}$$

The valuable improvement made by Wijs[1] produces an iodine solution which holds its standard strength for a very much longer period than the original Hubl solution, and also acts much more rapidly. The same results are eventually obtained as in the original Hubl process when the latter is carefully performed.

The method proposed by Wijs is the use of a solution of iodine monochloride in strong acetic acid, in place of the mixture of iodine and mercuric chloride. The original acid used was of 95 per cent. strength, but a much better solution is obtained by using acid of not less than 99 per cent.

Wijs admits a decrease of about 0·3 per cent. in 96 hours when using very pure 95 per cent. acid, but Lewkowitsch found it amounted to 4 per cent. in 64 hours. This Wijs attributed to the use of a less pure acid than was used by himself. However, the substitution of the stronger acid seems to settle the difficulty completely. Lewkowitsch states that he has found with 99 per cent. acid the same strength remains for two months; other operators have not found it quite so permanent as this, but all agree that it does not alter so as to cause inconvenience. So far as the weakening of the acetic acid iodine solution is concerned, A. Marshall[1] is of opinion that it must largely depend upon the amount of chloracetic acid formed in preparing the solution. Wijs himself is of opinion that if the acid is pure, and especially free from oxidizable matters, there should theoretically be no possibility of any diminution of strength.

---

[1] *Berichte*, 1898, **31**, 750.

The preparation of Wijs' iodine solution is carried out as follows: (*a*) 13 gm. of pure iodine are dissolved in a litre of 99 per cent. acetic acid; the strength is then determined by standard thiosulphate, then chlorine gas, washed and dried, is passed into it until the titer is doubled. With a little practice the proper ending of the chlorination is ascertained by the change of colour from dark brown to light yellow. If the gas is passed in until this just occurs the first titration may be dispensed with. Or (*b*) solutions of 7·9 gm. of iodine trichloride and 8·7 gm. of iodine respectively in glacial acetic acid (using about 400 c c. for each) are made up by warming on the water-bath, taking care that no moisture from the air is absorbed. The glacial acetic acid must be pure (it must give no green tinge when warmed with potassium dichromate and concentrated sulphuric acid). The two solutions are poured into a dry litre flask and made up to the mark with glacial acetic acid.

$$ICl_3 + I_2 = 3ICl.$$

(Method (*a*) is the cheaper of the two.)

The process of titrating the fat is carried out precisely as above described, with the exception that the time required for the absorption is very greatly curtailed. J. Lewkowitsch states that in the case of fats and non-drying oils the absorption of iodochloride is complete after half an hour, in the case of semi-drying oils after about an hour, and in the case of drying oils and marine animal oils in from 2 to 6 hours, according to the unsaturation of the glycerides. Lewkowitsch[2] strongly recommends Wijs' process. He finds it preferable to the Hübl iodine solution in almost every case, as it is infinitely superior to the latter as regards stability. He has known a solution to keep its strength practically unchanged for 5 months. It can be prepared rapidly, and the time spent on the test is very much shortened. It is not necessary to carry out a blank test in every case. Wijs' solution should be made at least 24 hours before it is required.

The results obtained by Wijs' method are generally higher than those given by Hübl's process, this being most noticeable in the case of the highly unsaturated oils. The results obtained by Wijs with purified allyl alcohol point to his method giving more correct figures than the Hübl process.[3]

---

[1] *J. S. C. I.*, 1900, **19**, 213.
[2] *Oils, Fats, and Waxes*, 4th Edition, Vol. I., p. 323.
[3] Allen, *Commercial Organic Analysis*, 4th Edition, Vol. II., p. 32.

PHENOL.

$C_6H_5OH = 94\cdot048.$

The chief volumetric method of determining phenol is that of W. F. Koppeschaar,[1] which is based on the formation of tribromophenol, as a snow-white crystalline precipitate, when bromine water is added in moderate excess to an aqueous solution of phenol, thus

$$(1)\ C_6H_5OH + 3Br_2 = C_6H_2Br_3OH + 3HBr.$$

The same author's[2] modification of this method, in which a mixture of alkali bromide and bromate is used instead of bromine water, and from which the bromine is liberated by hydrochloric acid, is now generally used, the reaction being as follows:–

$$(2)\ 5NaBr + NaBrO_3 + 6HCl = 6NaCl + 3Br_2 + 3H_2O.$$

The bromine thus set free, and not fixed by the phenol as shown in equation (1), is then determined by adding potassium iodide and titrating the liberated iodine with $^N/_{10}$ thiosulphate:–

$$(3)\ 2KI + Br_2 = 2KBr + I_2.$$
$$(4)\ I_2 + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI.$$

The following solutions are required:—

(*a*) Solution of sodium bromide and bromate ($5NaBr + NaBrO_3$). Pipette 100 c.c. of $^N/_1$ NaOH into a beaker, add bromine till the liquid becomes brown in colour and smells distinctly of bromine, then heat the liquid till it becomes quite colourless. Cool and dilute to 1 litre.

1 c.c. = 0·007992 gm. bromine
= 0·001568 gm. phenol.

Hence

$$\text{Iodine} \times \left(\frac{15\cdot68}{126\cdot92} = \right)0\cdot1235 = \text{phenol.}$$

Or (*b*) Make a $^N/_{20}$ solution of potassium bromide by dissolving 5·951 gm. in a litre of water, and a $^N/_{100}$ solution of potassium bromate by dissolving 1·670 gm. in a litre. 50 c.c. of each of these solutions are used in a determination and from the mixture 0·24 gm. of bromine will be liberated by acid, this amount being capable of converting 0·047 gm. of phenol into tribromophenol. Both of these solutions keep indefinitely.

NOTE.—Although tribromophenol bromide may be a constituent of the precipitate obtained in the above process, thus:

$$C_6H_5OH + 4Br_2 = C_6H_2Br_3OBr + 4HBr,$$

this is of no consequence, as this body is converted into the compound containing 3 atoms of bromine when potassium iodide is added to the acid solution:

$$C_6H_2Br_3OBr + 2KI + 2HCl = C_6H_2Br_3OH + 2KCl + 2HBr + I_2.$$

---

[1] *Z. a. C.*, 1876, **15**, 233.

[2] This has been attributed to Allen, whereas, as a matter of fact, it was given in Koppeschaar's original paper. See *Analyst*, 1877, **1**, 117.

The method of procedure is best shown by an example.

EXAMPLE.—5 gm. carbolic powder are put into a 250 c.c. flask, HCl added, and made up to the mark with water. The flask is shaken and the contents filtered. 50 c.c. of the filtrate (= 1 gm. of sample) are measured into a stoppered bottle and 100 c.c. of the bromide and bromate solution added, together with a little more HCl, and, after being well shaken, allowed to stand for 15 minutes. KI solution is then added, the bottle again shaken, and the iodine set free titrated with $^N/_{10}$ thiosulphate. Suppose that 13·8 c.c. of the latter are required, and that titration with iodine showed that 1 c.c. of it = 0·0121 gm. iodine; also that 10 c.c. of the bromide and bromate solution and KI required 10·5 c.c. thiosulphate. Then 100 c c. of the bromide and bromate solution = 105 c.c. $^N/_{10}$ thiosulphate of which 105 – 13·8 = 81·2 c.c. represent the bromine absorbed, which has been determined in terms of iodine.

Hence 81·2 × ·0121 × ·1235 = ·1214 gm. phenol or 12·14 per cent.

W. H. Coleman[1] says of Koppeschaar's method: "This process is accurate whenever solutions of pure carbolic acid, or mixtures from which the pure acid can be separated, are to be tested, but it fails in all cases (e.g. crude carbolic acid) when other phenols, particularly cresols, are also present".

The following modification of the above process is included in the United States Pharmacopœia. -

1·556 gm. of the sample is dissolved in water and made up to 1000 c.c. After well mixing, 25 c.c. (= 0·0389 gm. of phenol) are pipetted into a 200 c.c. stoppered bottle and 30 c.c. of the $^N/_{10}$ bromine solution added; then 5 c.c. of HCl are added, followed immediately by 5 c.c. of potassium iodide solution (20 per cent.). The mixture is shaken, the stopper and neck of the bottle rinsed with a little water, allowing the washings to run into the bottle, 1 c.c. of chloroform added, and the mixture well shaken. The liberated iodine is titrated with $^N/_{10}$ sodium thiosulphate, of which the number of c.c. used (which should not exceed 6) subtracted from 30 and the remainder multiplied by 4 gives the percentage of absolute phenol present in the sample.

NOTE. - The reason for adding 1 c.c. of chloroform in the above process is as follows: It often happens that the liquid, after being decolorized by thiosulphate, acquires a blue colour on standing. This is said to be caused by bromine (or iodine?) being retained by the oily tribromophenol, and only slowly dissolving in the supernatant fluid. By the addition of a little chloroform towards the end of the reaction, the precipitated tribromophenol is dissolved and the final point of the titration can be more readily observed.

Messinger and Vortmann[2] describe a method of determining phenol based on the fact that iodine combines with phenol in alkaline solution in the proportion of 6 atoms I to 1 mol. phenol.

METHOD OF PROCEDURE:—2 to 3 gm. phenol are dissolved in caustic soda solution (3 eq. NaHO to 1 eq. phenol) and made up to 500 c.c. with water; 10 c.c. of this are placed in a flask, warmed to 60° C., and $^N/_{10}$ iodine added until the solution is faintly yellow, with formation of a red precipitate. When cold, the solution is acidified with dilute H_2SO_4, made up to 500 c.c. and filtered. In 100 c.c. of the filtrate, the excess of I is titrated with $N/_{10}$ thiosulphate; this amount, deducted from the total I used, gives the amount absorbed by phenol, which, when multiplied by 0·1235, gives amount of phenol in the sample.

---

[1] Thorpe's *Dictionary of Applied Chemistry*, Vol. I., p. 659.

[2] *Berichte*, 1890, 2753, and *J. S. C. I.* 1890, 9, 1070.

This method has been carefully studied by J. M. Wilkie[1] who has worked out the following improved procedure: To the dilute phenol solution equal volumes of $N/_{10}$ iodine and sodium carbonate solutions are added. After 5 minutes, excess of sulphuric acid is added and the residual iodine titrated with $N/_{10}$ sodium thiosulphate and starch. Should too little iodine have been added, this is indicated by pronounced fading of the brown colour due to the iodine, and in extreme cases by precipitation of tri-iodophenol. In such cases more iodine and sodium carbonate solutions are to be added, and after 5 minutes' standing the determination is completed as above. Generally the amount of iodine added should be about double that required for the reaction. Stoppered bottles should be used, and the whole operation carried out in the cold.

SALICYLIC ACID.

(Ortho-hydroxybenzoic acid.)

$C_6H_4(OH)COOH = 138·048$.

Several methods have been proposed for the determination of this substance as existing in the form of salts or in a free state, and a critical examination of the most hopeful of these has been carefully made by W. Fresenius and L. Grünhut.[2] The experiments were made on pure sodium salicylate. The method proposed by Messinger and Vortmann in which it is said by the authors that 1 mol. of salicylic acid consumes 6 atoms of iodine was not confirmed in these experiments, and they came to the conclusion that the method could not be relied on to give even approximately correct results. On the other hand their experience of Freyer's[3] bromine method was that it gave satisfactory results.

Freyer's method is based on the fact, proved by A. H. Allen and other observers, that salicylic acid in aqueous solution ultimately reacts with 6 atoms of bromine ($3Br_2$) to form a tribrominated salicylic acid.[4]

Hence 138·048 gm. salicylic acid correspond to 479·52 gm. bromine.

Solutions Required.—(*a*) Solution of sodium bromide and bromate ($5NaBr + NaBrO_3$), made by dissolving 19·5 gm. (= 6·5 c.c.) of bromine in about 100 c.c. of water containing 10 gm. of sodium hydroxide. The liquid thus obtained is boiled well and then diluted to 2 litres. The solution keeps indefinitely.

0·138 gm. of salicylic acid corresponds to 0·480 gm. of free bromine, or as much as will be liberated by acid from about 50 c.c. of the solution.

---

[1] *J. S. C. I.*, 1911, **30**, 398.

[2] *Z. a. C.*, 1899 **38**, 292, also *Analyst*, 1900, **25**, 19.

[3] *Chem. Zeit.*, 1896, **20**, 820.

[4] For a discussion as to the composition of this compound, which is uncertain, see E. Werner, *Bull. Soc, Chim.*, 1886 [ii], **46**, 275.

(*b*) $^N/_{10}$ sodium thiosulphate (24·822 gm. of the crystals per litre). 1 c.c. = 0·008 gm. bromine.

METHOD OF PROCEDURE: First make a solution of the sample in water (preferably with the aid of a little NaOH), and for each determination measure out a volume corresponding to about 0·1 gm. of salicylic acid and dilute with water to about 100 c.c. Next, pipette a known volume, usually 50 or 60 c.c., of the bromide and bromate solution (*a*) into a stoppered bottle, add 5 c.c. of strong HCl, then the 100 c.c. of the solution of the sample as above.

It is essential that a volume of the bromide and bromate solution should be used sufficient to give about 75 per cent. of bromine in excess of that entering into the reaction. The bottle is stoppered, well shaken, and allowed to remain in the dark for at least 1 hour to ensure the completion of the reaction. Another bottle containing an equal quantity of the bromine solution is similarly diluted and acidified, and left to stand side by side with the sample. Potassium iodide solution (10 per cent.) is then added to the contents of both bottles, and the liberated iodine titrated with $^N/_{10}$ thiosulphate. Starch liquor may be added towards the end of the process, but it is important not to do so until the liquor is nearly decolorized.

The percentage of salicylic acid thus found in the same sample of pure sodium salicylate varied in four determinations from 86·21 to 86·43 per cent. The theoretical amount is 86·23 per cent.

The above process is specially valuable in presence of benzoic acid, which is not acted on by bromine in aqueous solution. The precipitate may be filtered off, and the benzoic acid isolated from the filtrate.

This method is not applicable to the analysis of mixtures of starch and sodium salicylate such as occur in medicinal tabloids. In such cases the substance should be dissolved in 90 per cent. alcohol, the solution brought to a definite volume, filtered from the undissolved starch, and an aliquot part of the filtrate used for the analysis. In a mixture of 90·91 per cent. of sodium salicylate and 9·09 per cent. of starch, the authors found in this way 89·97 per cent. of the former.

In the analysis of wines which contain sulphurous acid, aldehyde, and other substances which act upon bromine, the best method of determining salicylic acid, when present, is to make the liquid alkaline, concentrate it, render it acid, and extract it with a mixture of ether and petroleum spirit. The extract thus obtained is shaken with alkaline water, which removes the salicylic acid, and this aqueous solution can then be used in the bromine method.

Determination of Salicylic Acid in Beer.—The following process devised by F. T. Harry and W. R. Mummery[1] gives satisfactory results: 100 c.c. of the beer are placed in a flask marked at 200 c.c., made alkaline with 5 c.c. roughly $^N/_1$ NaOH, and all the alcohol driven off; this should be done at a temperature just below the boiling-point, as vigorous boiling appears to cause loss even when the solution is alkaline. After cooling, 5 c.c. of roughly $^N/_1$ HCl are added, and then at least 20 c.c. of a saturated solution of basic lead acetate; the whole is then made alkaline with about 20 c.c. of N/1 NaOH, and made up to the mark. At this stage the whole may be raised to boiling and allowed to cool before filtering, but this may be omitted if thought advisable. 100 c.c. of the filtrate are acidified with hydrochloric acid, the lead chloride precipitate is filtered off, and the filtrate extracted with ether three times. The ether is distilled off[1] and the salicylic acid dissolved in a small quantity of dilute alcohol and made up to 100 c.c. The salicylic acid is determined colorimetrically, after addition of a drop or two of dilute (neutral) ferric chloride solution, using ordinary Nessler glasses. For a standard, dissolve 0·01 gm. of pure salicylic acid in water in a 100 c.c. measuring flask and make up to the mark, then pipette 10 c.c. of the well-mixed solution into about 70 c.c. of water in a Nessler glass, add ferric chloride, make up to 100 c.c. and mix well. This standard is of convenient colour for comparison and contains 0·001 gm. of salicylic acid.

---

[1] *Analyst*, 1905, **30**, 124.

Wines are treated in the same way as beer, taking 50 c.c. of the sample, making up to 100 c.c., and filtering off 50 c.c. As with beer, it was necessary to add a large excess of lead acetate, and to have the whole fairly alkaline, in order to exclude all tannin bodies from the filtrate. For *preserved fruits, fruit pulps or jams* proceed as follows: 50 gm. of the crushed sample are placed in an ordinary flask which has been marked at 300 c.c.; a small quantity of water is added, then 15 to 20 c.c. of saturated basic lead acetate solution, and the whole made alkaline by the addition of about 25 c.c. of roughly N/1 NaOH. Then 15 to 20 c.c. of roughly N/1 HCl are added, the contents of the flask made up to the 300 c.c. mark, well shaken, and filtered cold through Rhenish paper, 200 c.c. of the filtrate being collected. The filtrate is acidified with HCl, refiltered if necessary, and extracted three times with ether, etc., as above, the salicylic acid being dissolved in a small quantity of dilute alcohol, ferric chloride added, and the liquid made up to 100 c.c. with water.

The amount of salicylic acid found multiplied by three gives percentage.

NOTE.—The lead acetate used is a saturated solution made in the usual way by boiling with litharge. The (neutral) ferric chloride is made by dissolving washed ferric hydroxide in a quantity of hydrochloric acid insufficient to bring the whole into solution. A few drops of the supernatant solution are withdrawn by a dropping tube when required.

The Departmental Committee in their Report on Preservatives and Colouring Matters in Food (1901) recommend that salicylic acid be not used in a greater proportion than 1 grain per pint in liquid food and 1 grain per pound in solid food and that its presence in all cases be declared.

Methyl Salicylate.—$C_6H_4(OH).COO(CH_3)$.—E. Kremers and M. M. James[2] have slightly modified the method proposed by Ewing and boil a weighed quantity of the substance with a known volume of normal alkali for 5 minutes. The excess of alkali is then titrated with normal acid, and the alkali consumed, multiplied by 0·152, represents the weight in grams of methyl salicylate.

---

[1] Or allowed to evaporate spontaneously at room temperature.

[2] *Chem. Centr.*, 1898, 1070.

The method proposed by Messinger and Vortmann is also recommended. 5 gm. of the sample are saponified with excess of alkali, and when cold diluted to 500 c.c.; 10 c.c. of this are heated, 50 c.c. of $N/_{10}$ iodine solution added, and the liquid diluted to 500 c.c.; in 100 c.c. of this, the excess of iodine is determined by means of $N/_{10}$ sodium thiosulphate. 1 c.c. of iodine solution absorbed, when multiplied by 0·002535, represents the amount of methylic salicylate, as 1 mol. of the ethereal salt absorbs 6 atoms of iodine.

Sodium di-iodosalicylic iodide is formed thus –

$$C_6H_4(OH).COONa + 3NaOH + 3I_2 =$$
$$C_6H_2I_2(OI)COONa + 3NaI + 3H_2O.$$

SUGARS AND STARCH.

SUGARS and starch belong to the large class of organic bodies known as carbohydrates, which are divided into the following principal groups:–

1. Monosaccharides. These have the empirical composition CH_2O, the most important being those containing 5 or 6 atoms of carbon.

(*a*) Pentoses, $C_5H_{10}O_5$, e.g. arabinose, xylose.

(*b*) Hexoses, $C_6H_{12}O_6$, including

(i) Dextrose, dextro-glucose, *d*-glucose, grape-sugar, starch-sugar (cryst., $C_6H_{12}O_6$, H_2O), which is found in the juice of most fruits, almost always accompanied by laevulose (the two hexoses being probably derived from sucrose), in honey, and in diabetic urine. It is formed on hydrolysing most of the known polysaccharides either with acids or enzymes.

(ii) Laevulose or *d*-fructose, found together with an equal amount of dextrose in honey and in many fruits. Inulin is completely converted into fructose on hydrolysis. (It is termed *d*-fructose, in spite of the laevo-rotation, to indicate that it belongs to the *d*-mannitol series.)

(iii) *d*-Galactose, which is produced, together with an equal proportion of dextrose, when lactose is hydrolysed by means of acids or enzymes.

All the above reduce Fehling's solution.

2. Disaccharides, $C_{12}H_{22}O_{11}$, including

(i) Sucrose or cane-sugar, which is found in the sugar-cane, beetroot, and maple.

(ii) Lactose or milk-sugar (cryst., $C_{12}H_{22}O_{11}$, H_2O), which is found in the milk of all mammals.

(iii) Maltose (cryst., $C_{12}H_{22}O_{11}$, H_2O), which, together with dextrins, is produced by the action of diastase (usually malt extract) on starch paste.

Lactose and maltose reduce Fehling's solution, but to a less degree than the hexoses. Sucrose does so only after hydrolysis.

All the members of this group are hydrolysed by heating with dilute mineral acids or by the action of enzymes, such as diastase (in malt), invertase (in yeast), and ptyalin (in the saliva). Sucrose in this way becomes converted into a mixture of dextrose and laevulose in equal numbers of molecules, the process being known as "inversion" and the product "invert sugar," as the dextro-rotatory cane-sugar solution becomes the laevo-rotatory mixture. By hydrolysis lactose is converted into dextrose and galactose; maltose into dextrose alone.

3. Polysaccharides $(C_6H_{10}O_5)_n$, including

(i) Cellulose, which forms the fundamental material of the structure of plants, and of which cotton, wood, etc., mainly consist.

(ii) Starch or amylum, which is present in the grains of cereals, in potatoes, etc.

(iii) Glycogen, the reserve carbohydrate of the animal organism, in which it appears to take the place of starch. It is present in the liver up to 10 per cent. and in muscle.

(iv) Dextrins, which are produced (*a*) by heating dry starch to 212° to 275°; (*b*) together with dextrose by boiling starch with dilute sulphuric acid; (*c*) together with maltose by the action of diastase on gelatinized starch. The various forms of dextrin are distinguished by their behaviour with iodine, erythrodextrin giving with this reagent a reddish-brown colour, achroodextrin no colour at all.

None of the above reduce Fehling's solution.

By the action of dilute sulphuric acid starch, glycogen, dextrins, and cellulose are ultimately hydrolysed to dextrose.

Dextrose, fructose, and invert sugar are fermentable by all yeasts. Cane-sugar, maltose, lactose, melibiose, and raffinose are fermentable only after inversion by dilute acids or by an appropriate enzyme.

Inversion of Cane-sugar.—If pure and dry cane-sugar is used, the following process yields a solution of invert sugar containing exactly 1 gm. in 100 c.c. 9·5 gm. of the cane-sugar are dissolved in 700 c.c. of hot water, 20 c.c. of $N/_1$ hydrochloric acid added, the mixture heated for 30 minutes at 100° in a water-bath, 20 c.c. of $N/_1$ soda solution added, and the cooled solution diluted to 1 litre. In the determination of sucrose in a mixture of sugars (e.g. commercial invert sugar) the following method is adopted. A 10 per cent. solution of the sample is made and 10 c.c. of this transferred to a flask, with the addition of 100 c.c. of water and 20 c.c. of $N/_2$ hydrochloric acid. The mixture is raised to the boiling-point and maintained at that temperature for one minute. It is then cooled, neutralized by the addition of 20 c.c. of $N/_2$ sodium hydroxide, and made up to 1000 c.c. The solution is then ready for titration with 10 c.c. of Fehling's solution. (A. R. Ling.)

Where polarimetric observations are to be made, Herzfeld's modification of the Clerget method is used, the details being as follows:—

The half-normal weight (i.e. 13 gm.) of sucrose is dissolved in 75 c.c. of water in a 100° C. measuring flask, 5 c.c. of hydrochloric acid (38 per cent.) added, a thermometer inserted in the flask, and the latter placed in a water-bath at 70° C. The flask is shaken continuously, and in this way the temperature is raised to 67° to 70° C. in about 2½ minutes, after attaining which it is kept constant for an additional 5 minutes, when it is rapidly cooled and polarized. A. R. Ling states that by this method sucrose may be determined with a fair degree of accuracy in presence of dextrins, malto-dextrins, maltose, lactose, or glucose, or of mixtures of these.

Preparation of Sugar Solutions for Titration by Fehling's Method.—The following reagents are used for the clarification of dark coloured or turbid sugar solutions:—

Basic Lead Acetate.—150 gm. of lead acetate in fine crystals is mixed in an evaporating basin with 45 gm. of litharge and 25 c.c. of water. This paste is allowed to remain at the room temperature for 2 to 3 hours with frequent stirring. At the end of this time the lead acetate and most of the litharge will have gone into solution. The basin and contents are, however, warmed on a piece of wire gauze or a sand-bath. The cream, which is now quite limpid and colourless, is poured into 500 c.c. of water and allowed to stand until the small amount of undissolved residue settles out. The solution (sp. gr. about 1·2) should be filtered.[1]

The amount of the above to be used for polarimetric observations varies with the kind of sugar. The purest centrifugal sugars require only from 0·5 to 2 c.c.; darker products require up to 10 c.c., whilst molasses require much more. It should be noted that laevulose is partially precipitated (and also dextrose, but to a lesser extent) by basic lead acetate.

Alumina Cream.—Pour a cold 2 to 3 per cent. solution of alum into dilute ammonia (sp. gr. 0·98); the converse method of precipitation yields an unsatisfactory granular product. The liquid and precipitate are transferred to a half-gallon bottle and the alumina allowed to subside. It is then washed in the bottle by decantation twice a day until the supernatant liquid gives no reaction with barium chloride. This usually takes about a week.

The volume of the above to be used for the normal solution (in saccharimetry) is about 5 c.c.

Ling states that "Purified animal charcoal has been used for decolorizing sugar solutions, but the error introduced by the adsorption of sucrose is considerable".

Although traces of lead are of little consequence in sugar solution prepared for polarimetric observations, it is of great importance to remove all lead when using the volumetric method. For this purpose anhydrous sodium carbonate or sodium sulphate is frequently used.

According to E. F. Armstrong[2] the following method of clarification is very efficient even under extremely unfavourable conditions. The normal quantity of sugar is dissolved in about 50 c.c. of water in a flask holding 100 c.c. According to the quality of the sample the solution will be (1) colourless but cloudy, (2) yellow, (3) brown, or (4) almost black. In the first case, add about 3 c.c. of alumina cream and one drop of basic lead acetate solution. In the second case, the same volume of alumina cream may be used, but the lead solution increased to 3 or 5 drops. In the third or fourth case, add about 2 c.c. of a 10 per cent. solution of sodium sulphate, and then the lead solution gradually, with constant shaking, till no further precipitate is produced. Whichever mode of clarification is adopted, the liquid is well agitated and allowed to stand at rest for a few minutes, to ensure the complete separation of any precipitate. The flask is then filled nearly to the mark with water and the froth allowed to rise to the surface, when it is destroyed by the cautious addition of a few drops of spirit or a single drop of ether. Water is then added exactly to the mark, the contents of the flask thoroughly mixed by agitation, and the liquid filtered through a dry filter.

---

[1] A. R. Ling in Thorpe's *Dictionary of Applied Chemistry*, v., 238.

[2] Allen's *Commercial Organic Analysis*, vol. i. (1909).

Pellet has shown that the errors introduced by clarifying sugar solutions, with basic lead acetate, viz., concentration owing to the volume occupied by the precipitate, and diminution owing to sugar mechanically retained by the precipitate, compensate each other and there is no necessity to make any correction.

Horne proposed the use of anhydrous basic lead acetate, which has been found to give excellent results.

1. The Determination of Reducing Sugars by Fehling's Method.

Preparation of Fehling's Solution.—**Solution No. 1.**—Dissolve 69·28 gm. of pure recrystallized copper sulphate in water and make up to 1 litre.

Solution No. 2.—346 gm. of crystallized Rochelle salt are dissolved in hot water in one beaker, 142 gm. of sodium hydroxide are dissolved in water in another beaker, the two solutions are then poured into a litre flask, cooled, and made up to the mark.

Equal volumes of these solutions are accurately measured out immediately before use and mixed, the mixture constituting Fehling's solution.

The method of procedure now to be described is that recommended by Ling and Rendle[1] and by Ling and Jones,[2] by which results are obtained equal in accuracy to the gravimetric method of Brown, Morris, and Millar.[3] The average error is 1 in 300. The principal points in the method are that the titration is performed in a boiling flask on 10 c.c. of *undiluted* Fehling's solution, and that ferrous thiocyanate is used as indicator.

The indicator is prepared by dissolving 1 gm. of ferrous ammonium sulphate in 10 c.c. of cold water, adding 1·5 gm. of ammonium thiocyanate, and, when this has dissolved, 2·5 c.c. of concentrated hydrochloric acid. The solution so obtained has invariably a red colour, due to the presence of ferric salt which is readily reduced by addition of a trace of zinc dust. The indicator when kept for some hours develops the red coloration by atmospheric oxidation and must again be reduced. In practice it is found that the freshly prepared indicator is too sensitive, and that it is most useful after it has been reduced twice with zinc dust. The method of titration is as follows. Freshly mixed Fehling's solution (10 c.c.) is accurately measured into a 200 c.c. boiling flask and raised to boiling. The sugar solution, which should be adjusted to such a strength that 20 to 30 c.c. of it are required to reduce 10 c.c. of Fehling's solution, is then run into the boiling liquid in small amounts, commencing with 5 c.c. After each addition of sugar solution, the mixture is boiled, the liquid being kept rotated. About a dozen drops of the indicator are placed on a porcelain or opal glass slab, and when it is judged that the precipitation of cuprous oxide is complete, a drop of the liquid is withdrawn by a clean glass rod or by a capillary tube, and brought in contact with a drop of the indicator on the slab. The test must be carried out rapidly. It is also essential to perform the titration as rapidly as possible, as an atmosphere of steam is then kept in the neck of the flask, and the influence of atmospheric oxygen avoided. At the final point, the liquid is boiled for about 10 seconds. Duplicate titrations should agree to 0·1 c.c. The only defect of this indicator is that it cannot be used with products containing ferric iron. The titration can be carried out by artificial light.

---

[1] *Analyst*, 1905, **30**, 182; 1908, **33**, 167.

[2] *Ibid.*, 1908, **33**, 160.

[3] *J. Chem. Soc. Trans.*, 1897, 71, 112.

To standardize Fehling's solution, Ling and Rendle (loc. cit.) dissolve pure sucrose (0·95 gm.) in water (150 c.c.), and boil for one minute with $N/_2$ hydrochloric acid (30 c.c.). After cooling the solution is neutralized with $N/_2$ sodium hydroxide (30 c.c.) and made up to 500 c.c. This solution contains 0·2 gm. of invert sugar per 100 c.c., and about 25·6 c.c. should be required for 10 c.c. of Fehling's solution, but, of course, the exact value of the latter is always determined. It is then titrated as above against 10 c.c. of Fehling's solution. The relative amounts of anhydrous invert sugar, dextrose, and maltose required to reduce a fixed volume of Fehling's solution are 100 : 96 : 161; but in the case of the first two sugars the ratio varies somewhat with concentration. Ling and Jones[1] give a table to correct for this. It may be required in the analysis of commercial invert sugar when the percentage of dextrose and of laevulose are separately reported.

The table on p. 414 by Ling and Jones will be found a great time-saver in obtaining results by this method.

Pavy's Modified Fehling Process.

In the early days of the use of Fehling's solution the end point in the titration was determined by the disappearance of the blue colour—a difficult matter to observe when a dark coloured physiological liquid was being examined. To obviate this and other difficulties F. W. Pavy (1879) proposed to employ a copper solution containing sufficient ammonia to keep the reduced cuprous oxide in solution. The method has been applied specially for the determination of dextrose in urine. Many physiological liquids, however, are so dark coloured as to render impossible any accurate determination by this method.

Pavy's solution is prepared as follows :—

Solution A. 34·65 gm. of recrystallized copper sulphate are dissolved in water and made up to 500 c.c.

Solution B. 170 gm. of Rochelle salt and 170 gm. of potassium hydroxide are dissolved in water in separate beakers and the solutions poured into a 500 c.c. measuring flask. This is then cooled and made up to the mark with water.

60 c.c. of each of the above solutions are measured into a litre flask, 300 c.c. of 0·880 ammonia is added and the liquid made up to the mark with water. This is Pavy's solution, and 20 c.c. are reduced by 0·01 gm. of glucose. If other sugars are to be determined, the titre of the solution must be established for each of these.

METHOD OF PROCEDURE: A round-bottomed flask of 150 c.c. capacity is provided with a doubly bored rubber stopper. Through one opening in the stopper the delivery end of the burette passes and through the

---

[1] (Loc. cit., 165.)

Ling and Jones's Table for use with Fehling's Solution.[1]

Volume of Sugar Solution required by 10 c.c. of Fehling's Solution.	Dextrose.		Laevulose.		Invert Sugar.		Maltose.	
	D Dextrose in 100 c.c. of Solution.	D'. Fehling's Solution equivalent to 1 gm. of Dextrose	L. Laevulose in 100 c.c. of Solution.	L'. Fehling's Solution equivalent to 1 gm. of Laevulose.	I. Invert Sugar in 100 c.c. of Solution.	I'. Fehling's Solution equivalent to 1 gm. of Invert Sugar.	M Maltose in 100 c.c. of Solution.	M'. Fehling's Solution equivalent to 1 gm. Maltose.
c.c.	gm.	c.c.	gm.	c.c.	gm.	c.c.	gm.	c.c.
20	0·2427	206·0	—	—	—	—	—	—
21	0·2332	205·1	—	—	0·2412	197·5	0·3888	122·5
22	0·2226	204·2	0·2411	188·5	0·2311	196·8	0·3711	A constant
23	0·2138	203·4	0·2312	188·0	0·2218	196·0	0·3550	
24	0·2056	202·6	0·2222	187·5	0·2132	195·5	0·3402	
25	0·1981	201·9	0·2138	187·1	0·2052	194·9	0·3266	
26	0·1911	201·3	0·2060	186·7	0·1980	194·3	0·3140	
27	0·1846	200·7	0·1988	186·3	0·1910	193·9	0·3023	
28	0·1784	200·1	0·1921	186·0	0·1846	193·4	0·2915	
29	0·1728	199·6	0·1857	185·6	0·1787	193·0	0·2815	
30	0·1675	199·1	0·1798	185·4	0·1731	192·5	0·2721	
31	0·1625	198·6	0·1743	185·1	0·1678	192·2	0·2633	
32	0·1577	198·2	0·1691	184·8	0·1629	191·8	0·2551	
33	0·1532	197·8	0·1642	184·6	0·1583	191·5	0·2474	
34	0·1490	197·4	0·1596	184·3	0·1539	191·2	0·2401	
35	0·1450	197·0	0·1552	184·1	0·1497	190·9	0·2332	
36	0·1412	196·7	0·1511	183·9	0·1458	190·6	0·2268	
37	0·1377	196·4	0·1472	183·6	0·1421	190·3	0·2206	
38	0·1343	196·0	0·1435	183·4	0·1385	190·1	0·2148	
39	0·1310	195·8	0·1399	183·3	0·1349	189·8	0·2093	
40	0·1279	195·5	0·1366	183·1	0·1319	189·6	0·2041	122·5
41	—	—	0·1334	182·9	0·1288	189·4	—	—
42	—	—	0·1298	182·8	0·1259	189·2	—	—
43	—	—	0·1274	182·6	—	—	—	—

Examples showing the use of the above table:—

(i) Suppose that 25·0 c.c. of a solution of pure laevulose are required to reduce 10 c.c. of Fehling's solution.

The figure in the column under L and opposite 25, viz. 0·2138, gives the percentage of laevulose in the solution.

(ii) Suppose that for 10 c.c. of Fehling's solution 32·7 c.c. of a solution of pure dextrose are required. Then the percentage of dextrose in the solution will be

$$0{\cdot}1577 - ({\cdot}1577 - {\cdot}1532) \times {\cdot}7 = 0{\cdot}1577 - 0{\cdot}0032 = 0{\cdot}1544.$$

(iii) The numbers given in columns D', L', I', and M' are used when separate determinations of two reducing sugars in a mixture, e.g. commercial invert-sugar, are required. In these cases polarimetric observations are necessary, in addition to the determination of cupric-reducing power. A fully worked-out example of the calculation of percentages of dextrose and laevulose respectively from data so obtained is given in the *Analyst*, 1908, **33**, 166 *et seq.*

---

[1] Given in the *Analyst*, 1908, **33**, 165. The table was constructed on the basis of a preparation of Fehling's solution, of which 10 c.c. required 25·65 c.c. of a 0·2 per cent. solution of invert sugar.

other a glass tube bent twice at right angles, the latter being intended for the escape of the steam and to prevent the access of air. 40 c.c. of Pavy's solution are measured into the flask, and, after inserting the stopper, the solution is slowly raised to boiling. The liquid under examination is then run in from the burette at the rate of 60 to 100 drops per minute until the blue colour is nearly discharged. The addition is then continued drop by drop until the last trace of blue has disappeared, this being most readily observed when a sheet of white paper or a plate of opal glass is placed behind the flask.

Gerrard's Cyano-cupric Process.

This process, as improved by Gerrard[1] and A. H. Allen, has proved a valuable addition to the processes of titration based on the reducing power of glucose. It has the advantage over Pavy's method in causing no evolution of ammonia; moreover, the reduced solution is reoxidized so slowly that titration may with reasonable expedition even be conducted in an open dish. The process is based on the following facts: When a solution of potassium cyanide is added to a solution of copper sulphate a colourless stable double cyanide of copper and potassium is formed, thus:-

$$CuSO_4 + 4KCy = CuCy_2, 2KCy + K_2SO_4.$$

This salt is not decomposed by alkalis, hydrogen sulphide, or ammonium sulphide. If potassium cyanide be added to Fehling's solution the latter is decolorized, the above double salt being formed at the same time, and if the colourless solution be boiled with glucose no cuprous oxide is precipitated. If there be present excess of Fehling's solution over the amount capable of being decolorized by the potassium cyanide, the mixture is blue, and when it is boiled with a reducing sugar the extra portion is reduced, but no cuprous oxide is precipitated, the progress of the reduction being marked by the gradual and final disappearance of the colour of the solution, just as in Pavy's process.

PROCESS OF TITRATION: 10 c.c. of freshly made Fehling's solution, or 5 c.c. of each of the constituent solutions, are diluted with 40 c.c. of water in a porcelain dish and heated to boiling. An approximately 5 per cent. solution of potassium cyanide is added very cautiously from a burette or pipette to the still boiling and well agitated blue liquid till the colour is just about to disappear. Excess of cyanide must be carefully avoided.[2]

10 c.c. of Fehling's solution are now accurately measured into the dish, and the sugar solution (of about ½ per cent. strength glucose) run in slowly from a burette, with constant stirring and ebullition, till the blue colour disappears. Only the second measure of Fehling's solution suffers reduction. The volume of sugar solution run in contains 0·05 gm. of glucose.

---

[1] *Year Book Pharm.*, 1892, 400.

[2] As the double cyanide solution keeps for some time, a stock may be made up, so that 50 c.c. contain 10 c.c. of Fehling's solution, and that volume taken for each titration, instead of going through the process of exact decolorization every time.

Some technical applications of the Solutions to mixtures of various Sugars.

It cannot be claimed for these determinations that they are absolutely exact; but with care and practice, accompanied with uniform conditions, they are probably capable of the best possible results whatever methods may be used.

Cane-Sugar, Grape-Sugar, and Dextrin.[1]—The solution containing these three forms is first titrated with the usual Fehling solution for grape sugar. A second portion is boiled with acetic acid (which only inverts cane-sugar) and titrated. Finally, a third portion is completely hydrolysed with sulphuric acid and titrated. The difference between the first and second titrations gives the cane-sugar, and that between the second and third the dextrin.

Another method might be suggested as follows: First determine the grape-sugar by Fehling's solution. Next, convert the sucrose into invert-sugar by the action of invertase—the other constituents being unaffected—and determine the grape- and invert-sugars together by a second titration with Fehling. Finally, the solution is heated for some hours with dilute sulphuric acid, whereby the cane-sugar is inverted and the dextrin hydrolysed to dextrose: the solution is then titrated for the third time. The difference between the third and second titrations gives the dextrose-equivalent of the dextrin present. (Or the dextrin may be determined gravimetrically by pouring the aqueous solution into a large excess of rectified spirit in a weighed beaker. After standing till the precipitate is completely settled the liquid is poured off, and the dextrin weighed.)

Milk-Sugar and Cane-Sugar.—If the determination of milk-sugar is alone required, and by the usual Fehling solution, the casein and albumen must first be removed. Acidify the liquid with a few drops of acetic acid, warm until coagulation is effected, and filter. Boil the filtrate to coagulate the albumen. Filter again, and neutralize with soda previous to treatment for sugar by the copper test. The number of c.c. of Fehling's solution required, multiplied by 0·006786, will give the weight of milk-sugar in grams. Direct determination by Pavy-Fehling is preferable to this method. Cane-sugar in presence of milk-sugar may be determined as follows: Dilute the milk to ten times its bulk, having previously coagulated it with a little citric acid, filter, and make up to a definite volume, titrate a portion with Pavy-Fehling solution, and note the result. Then take 100 c.c. of the filtrate, add 2 gm. of citric acid, and boil for 10 minutes, cool, neutralize, make up to 200 c.c., and titrate with copper solution as before. The difference between the reducing powers of the solutions before and after inversion is due to the cane-sugar, the milk-sugar not being affected by citric acid.

Stokes and Bodmer[2] have experimented largely on this method, and with satisfactory results. The plan adopted by them is to use 40 c.c. of Pavy-Fehling liquid (= 0·02 gm. glucose), and to dilute the sugar solution (without previous coagulation), so that from 6 to 12 c.c. are required for reduction. By using a screw-clamp on the rubber burette tube, the sugar solution is allowed to drop into the boiling liquid at a moderate rate. If Cu_2O should be precipitated before the colour disappears, a fresh trial must be made, adding the bulk of the sugar at once, then finishing by drops. If, on the other hand, the sugar has been run in to excess, which owing to the rather slow reaction is easily done, fresh trial must be again made until the proper point is reached; this gives the milk-sugar. Meanwhile a measured portion of the mixed sugar solution is boiled with 2 per cent. of citric acid for at least 30 minutes.[1] For example, suppose that 20 c.c. of milk had been diluted to 200 c.c., 50 c.c. of the latter should be boiled with 1 gm. of citric acid. The liquid is then neutralized with ammonia, made up to double its original volume, and titrated as before.

---

[1] Biard and Pellett, *Z. a. C.*, **24**, 275.

[2] *Analyst*, 1885, **10**, 62.

These operators have determined the reducing action of milk-, cane-, and grape-sugar on the Pavy-Fehling liquid, the result being that 100 lactose represents respectively 52 glucose or 49·4 sucrose.

F. W. Richardson and A. Jaffè[2] state that the copper method of determining mixtures of sugars in milk are practically valueless, having obtained far more consistent results by polarimetric methods.

STARCH.

THE general procedure followed in all methods for the determination of starch is as follows:—

(i) The extraction of the starch, either in a state of purity or after its decomposition into dextrin and maltose, or into dextrin, maltose, and dextrose; (ii) the determination of the amounts of these starch products.

A method frequently employed consists in the conversion of starch into dextrose by boiling with sulphuric or hydrochloric acid (2 per cent. or more) for some hours, either with or without pressure, and determining the dextrose produced by means of Fehling's solution. This process, even when most carefully conducted, is incapable of yielding anything like accurate results, these invariably coming out too low; on the one hand, from incomplete conversion to dextrose, and, on the other, through over conversion, giving rise to condensation products having either a much lower cupric-reducing power or none at all. Dextrose found multiplied by 0·9 gives starch.

Fairly good results are obtained by boiling the starch with dilute acid for ½ to 1 hour, or until a drop of the liquid gives no blue colour with iodine solution, and then determining the products of decomposition.

For the determination of starch in all the cereals, raw, as well as malted, O'Sullivan's method, involving the use of diastase, is undoubtedly the most trustworthy. Full details of this very elaborate method will be found in the *J. C. S.*, **45**, 1. This has been considerably simplified by the A. O. A. C., whose modified method is as follows:—

Extract 3 gm. of the finely powdered substance (ground in a coffee-mill kept clean for the purpose) on a hardened filter with five successive portions of 10 c.c. of ether (this removes fat, etc.), wash with 150 c.c. of

---

[1] The authors specified 10 minutes, but Watts and Tempany (*Analyst*, 1905, **30**, 119), have shown that 30 to 40 minutes' boiling is required.

[2] *J. S. C. I.*, **23**, 309.

10 per cent. alcohol (to dissolve out the sugars, the proteins other than casein, etc.), and then with a little strong alcohol. Place the residue in a beaker with 50 c.c. of water, immerse the beaker in a boiling water-bath, and stir the contents constantly for 15 minutes or until all the starch is gelatinized. Cool to 55°, add from 20 to 40 c.c. of malt extract, and maintain at this temperature until a microscopic examination of the residue with iodine reveals no starch. Cool, make up directly to 250 c.c., and filter. Place 200 c.c. of the filtrate in a flask with 20 c.c. of 25 per cent. HCl (sp. gr. 1·125), connect with a reflux condenser, and heat in a boiling water-bath for 2½ hours. Nearly neutralize whilst hot with sodium carbonate, cool, and make up to 500 c.c. Mix the solution well, pour through a dry filter, and determine the dextrose in an aliquot portion. Convert the dextrose into starch by the factor 0·9.

Prepare the malt extract by digesting 10 gm. of fresh, finely ground malt 2 or 3 hours at ordinary temperature with 200 c.c. of water and filtering bright. Ascertain the amount of dextrose in a given quantity of the filtrate after boiling with acid, etc., as in the starch determination, and make the proper correction.

TANNINS.[1]

The determination of tannin in the materials used for tannin is by no means of the most satisfactory character. Many methods have been proposed, and given up as practically useless. Lowenthal's method, with later variations, is accepted as the best volumetric method; but it is still deficient in accuracy and reliability, although much ingenuity and intelligence have been expended on it.

One difficulty is still unsurmounted, and that is the preparation of a pure tannic acid to serve as standard. The various tannins in existence are still very imperfectly understood,[2] but so far as the comparative analysis of tannin materials among themselves is concerned, the method in question is theoretically the best.

The principle of the method depends on the oxidation of the tannic acid, together with glucosides and other easily oxidizable substances, by permanganate, regulated by the presence of soluble indigo, prepared from what is commonly called indigo carmine, but is chemically sulphindigotate of sodium or potassium, which also acts as an indicator of the end of the reaction. The total amount of such substances having been found and expressed by a known volume of permanganate, the actually available tannin is then removed by gelatine, or by the hide-powder system, and the second titration is made upon the solution so obtained in order to find the amount of oxidizable matters other than tannin.

---

[1] Pure gallotannic acid or tannin from galls has the composition $C_{14}H_{10}O_9$, and in constitution is the anhydride of gallic acid, or digallic acid.

[2] Von Schroder, whose suggestions have been adopted by the German Association of Tanners, selects a commercial pure tannic acid for use as a standard by dissolving 2 gm. in a litre of water. 10 c.c. of this is titrated with permanganate as described. 10 c.c. are then digested 20 hours with 3 gm. moistened hide-powder. 50 c.c. of the filtrate from this is then titrated, and if the permanganate consumed amounts to less than 10 per cent. of the total consumed by the tannin, it is suitable for a standard. 1000 parts being considered equivalent in reducing power to 1048 parts of tannin precipitable by hide, according to Hammer's experiments, therefore Von Schroder, after titrating as described, calculates the dry matter, and multiplies by the round number 1·05 to obtain the value in actual tannin precipitable by hide.

The volume of permanganate so used, deducted from the volume used originally, shows the amount of tannin actually available for tanning purposes expressed in terms of permanganate.

H. R. Procter in his *Leather Industries Laboratory Book* gives the most recent methods of using this process in the Yorkshire College where he is the professor of leather manufacture, and gives his opinion of its value as a practical process. "It is now much superseded by the hide-powder method, but there are still a few cases in which it may be employed with advantage. Where only one or two analyses are to be made at one time, the preparation and adjustment of solutions is much more tedious than gravimetric analysis, but where a number of successive titrations are required it is considerably more rapid. It has the advantage that it can be applied direct to solutions however dilute, and if gelatine precipitation is used, it is much less affected by the presence of gallic acid or other fixed acids than the hide-powder method, and is therefore well adapted for the analysis of weak and waste liquors for technical purposes, for the systematic testing of spent tans, and for the analysis of sumach and myrabolans which contain much gallica cid, and which in the gravimetric method is wholly or partially estimated as tanning matter."

The extraction of the tannic acid from the raw material is best performed by making an infusion of the ground substance first with distilled water to about 500 c.c. at a temperature not greater than 50° C., then with water at 100° C., and percolating till free from tannin, and diluting when cold to 1 litre. Portions are filtered if necessary. Concentrated extracts are dissolved before titration by adding them to boiling water, then cooling and diluting to the measure. In the case of strong materials such as sumach or valonia 10 gm., or oak bark 20 gm., are used.

The quantity of these extracts to be used for titration must be regulated to some extent by the amount of permanganate required to oxidize the tannic and gallic acids present. Practice and experience will enable the operator to judge of the proper proportions to use in dealing with the various materials, bearing in mind that volumetric processes are largely dependent upon identity of conditions for securing concordant results. The recommendation of the best authorities is that the strength of the solution used for titration should be such as to give a solid residue of from 0·6 to 0·8 gm. from 100 c.c.

The working details, according to Procter, adopted at the Yorkshire College are as follows. The solutions required are:—

(1) Pure potassium permanganate, 0·5 gm. per litre. As very weak solutions do not keep well, it is best to make up one of 5 gm. per litre, and dilute when wanted. The exact strength of the permanganate is not important so long as it is constant through a series of experiments.

(2) Pure indigo-carmine 5 gm., and concentrated H_2SO_4, 50 gm. per litre. This must be filtered, and should give a pure yellow free from

any trace of brown where oxidized with permanganate; 25 c.c. of this solution should equal about 30 c.c. of the permanganate, and, if necessary, must be diluted to that strength.

(3) Solution of pure tannin, 3 gm. to 1 litre. Since absolutely pure tannin cannot be obtained, the following method is adopted: A sample of the purest obtainable tannin (not less than 90 to 95 per cent. pure by hide-powder) is preserved air-dry in a well-stoppered bottlé, and the moisture carefully determined. The principal impurity is gallic acid, which acts on permanganate like tannin, but reduces somewhat more strongly, and 1 part of such tannin, calculated to dry weight, is equal on the average to 1·05 parts of pure tannin. Hence it is easy to calculate a quantity of the air-dry tannin equal in permanganate value to 0·3 gm. of pure tannin, and this is weighed out when required and made up to 100 c.c. The moisture varies very little, but it is well occasionally to re-determine it and calculate afresh.

Method of Procedure: 25 c.c. of the indigo solution are mixed in a beaker with about ¾ litre of clean tap water, and the permanganate added drop by drop from a glass-tapped burette till a pure yellow is obtained, the liquid being stirred steadily the whole time. A disc stirrer or a glass rod bent several times back and forward, is to be preferred to a plain rod; or some method of mechanical stirring may be adopted. The dropping should be always as nearly as possible at a similar rate for each experiment, and should be slower towards the end of the titration. It is convenient to keep a second beaker titrated to a pure primrose yellow as a standard test. Titrations may be accurately performed by artificial light, but usually differ slightly from those by daylight, and hence the light should not be varied in the course of an analysis. For daylight work Kathreiner recommends the use of a white basin instead of a beaker. The permanganate solution is allowed to drop in, with constant stirring, till the pure yellow liquid shows a faint pinkish rim, most clearly seen on the shaded side. This end-reaction is of extraordinary delicacy, and is quite different from the pink caused by excess of permanganate, being an effect common to all pure yellow liquids. The titration is done at least twice, and the average taken; ¾ litre of water and 25 c.c. of indigo are then taken as before, and 5 c.c. of the tannin solution are added and similarly titrated repeatedly. Deducting amount required for the indigo, the remainder is that consumed by the tannin, which should not at most exceed two-thirds of that required by the indigo. A similar titration is made with the tannin infusion to be examined, of which such a number of cubic centimetres is employed as will consume about the same quantity of the permanganate as the standard tannin solution The value of the total astringent is then calculated in terms of tannin.

Since tanning matters contain astringents which are not taken up by the hide, but which are oxidized by permanganate like tannins, it is in most cases necessary to remove the tannin from a portion of the infusion, and to repeat the titration to determine the non-tannin ingredients.

This may be done by the hide-powder method at the same time that the tannin substance is determined gravimetrically, but a much quicker and even better method is that of Hunt. The solutions required are:—

(1) Pure gelatin, 2 gm. per 100 c.c.

(2) Saturated solution of NaCl containing 50 c.c. of concentrated H_2SO_4 per litre.

METHOD OF PROCEDURE: To 50 c.c. of the liquor (of about the strength of 1 to 1·5 gm. of tannin per 100 c.c.) are added 25 c.c. of the gelatin solution and 25 c.c. of the salt solution, and about a teaspoonful of kaolin or barium sulphate, and the whole is well shaken for 5 minutes and filtered. This filtrate, which should be perfectly bright, is titrated for non-tannin bodies by the permanganate method, double the volume being taken which was employed for determination of total astringents, and the result is deducted before calculating the tanning value.

It is impossible to give here the opinions held by various authorities on this subject, therefore the reader who desires fuller information should consult the various papers contributed to various journals, etc., and more especially Procter's book before mentioned.

The table on p. 422 by B. Hunt[1] is appended, as the result of careful working, and as a guide to the nature of various tanning materials.

The "total extract" in the table was determined by evaporating a portion of the tannin solution to dryness in a small porcelain basin and drying the residue at 110° C. The "insoluble matter" was also dried at 110° C.

The hide-powder process for tannin not being a volumetric one is not described here.

Tannin in Tea.—Tea-tannin is considered to be identical with the quercitannic acid ($C_{19}H_{16}O_{10}$) of oak bark.

R. R. Tatlock and R. T. Thomson,[2] after examining the various methods employed for the determination of tannin in tea and finding them unsatisfactory, fixed upon the following process after many trials:—

Boil 1 gm. of the tea in powder with 400 c.c. of water under a reflux condenser for 1 hour. Filter, wash with hot water, cool to 15·5°, or within 2° or 3° of that, and add a solution containing 1 gm. of ordinary basic quinine sulphate dissolved in a mixture of 25 c.c. of water and 2·5 c.c. of $N/_1 H_2SO_4$. Mix thoroughly and allow to stand for 10 to 15 minutes, when the tannin will have been brought down as quinine tannate, in the form of a pale brown flocculent precipitate. Collect this on a weighed filter, wash any precipitate in the beaker on to the filter with some of the filtrate, but do not wash with water. Let the filter drain, then transfer to a weighed dish and dry at 100°.

Quinine tannate × 0·75 = tannin.

The following results are recorded:—

	Tannin per cent.	
	Variations.	Average.
Indian teas . . .	13·32-14·98	14·33
Ceylon „ . . .	10·13-13·91	12·29
China „ . . .	7·27-10·94	9·50

---

[1] *J. S. C. I.*, 1885, **4**, 264.

[2] *Analyst*, 1910, **35**, 103.

Name of Material.	Total matters Oxidized by Permanganate, as Oxalic Ac.	Tannin, as Oxalic Ac. (Procter).	Tannin, as Oxalic Ac. (Hunt).	Total Extract.	Insoluble.
	per cent.	per cent.	per cent.	per cent.	per cent
English oak bark	15·70	13·54	11·97	18·38	66·15
Canadian hemlock bark	9·03	7·46	7·08	13·96	75·25
Larch bark	8·20	7·17	6·15	20·64	60·80
Mangrove bark	31·35	29·71	28·48	26·60	49·70
Alder bark	8·27	6·15	5·73	19·36	68·00
Blue gum bark	10·18	8·91	8·91	11·76	74·65
Valonia	37·41	35·24	30·50	38·50	46·05
Myrabolans	48·23	38·43	38·00	42·80	—
Sumach	42·53	34·30	31·46	41·10	47·77
Betel nut	15·91	13·87	13·79	17·94	67·00
Turkish blue galls	73·38	65·83	59·96	48·40	36·35
Aleppo galls	98·85	87·82	83·05	68·80	14·32
Wild galls	26·21	18·75	16·56	31·70	54·17
Divi-Divi	66·98	62·62	61·22	54·38	29·90
Balsamocarpan (poor and old sample)	50·49	37·76	32·88	57·14	28·25
Pomegranate rind	27·58	24·18	23·12	41·00	49·50
Tormentil root	22·27	20·98	20·68	19·70	67·95
Rhatany root	22·27	20·15	19·30	18·80	66·00
Pure Indian tea	23·06	18·65	17·40	34·46	53·40
Pure China tea	18·03	14·21	14·09	24·50	62·60
Cutch	57·65	51·95	44·24	61·60	4·75
Gum kino	66·39	59·55	51·55	79·30	1·00
Hemlock extract	35·16	33·17	30·98	48·78	—
Oakwood extract	33·49	26·90	23·86	37·78	—
Chestnut extract	39·77	32·63	28·88	50·28	
Quebracho extract	48·22	34·45	40·81	49·00	—
"Pure tannin"	135·76	122·44	121·93	—	—
Tan liquor, sp. gr. 1·030	4·84	3·14	2·10	6·01	—
Spent tan liquor, sp. gr. 1·0165	1·40	0·37	0·25	3·10	—
			Absorbed by Dry Pure Skin.		
Gambier, cube	70·12	—	51·07	74·40	5·31
,, sarawak	63·13	—	47·09	70·70	3·67
,, bale	56·00	—	43·70	63·54	1·40

NOTE.—The percentages of tannin given in the above table are expressed in terms of crystallized oxalic acid, since it is impossible to give the results of tannin determinations in actual percentages of tannin.

A. H. Allen[1] originated a method of determining tannin in tea based on the precipitation of the tannin from a hot solution by a standard solution of lead acetate, the end of the action being ascertained by filtering a few drops of the liquid, and testing it with ammoniacal ferricyanide. The method was selected partly because the determination included any gallic acid which might be present. For this reason the method is not suited for the assay of tanning materials without some modification. *Vide*, 10th edition, page 359.

---

[1] *C. N.*, **29**, 169, 189.

Tannin in Wine.—For this determination, A. Carpené recommends the use of a solution af ammonia-acetate of zinc containing a large excess of ammonia, which reagent has the property of forming with the Ænotannin, a tannate of zinc quite insoluble in water, in ammonia, and in excess of the reagent itself; while it gives no precipitate with alcohol, malic or tartaric acid, tartrates, glycerin, gelatin, albumen, or the iron salts of organic acids. With gallic and succinic acids, dextrose, and salts of aluminium it forms precipitates soluble in excess of the reagent and in ammonia.

On treating the wine with an excess of ammoniacal zinc acetate, a precipitate is formed, consisting of zinc tannate mixed with a small quantity of colouring matter. The wine is heated nearly to boiling to agglomerate the precipitate, which, after cooling, is filtered off and washed with a little boiling water, to remove adherent colouring matter. The precipitate is dissolved in dilute sulphuric acid, and the solution so obtained titrated with standard permanganate and indigo (see p. 420).

Ammoniacal Zinc Acetate Solution.—Dissolve 20 gm. of zinc acetate in 80 c.c. of water, and add 12 c.c. of ammonium acetate solution. The latter is made by neutralizing glacial acetic acid with strong ammonia. 8 c.c. of strong ammonia are then added.[1]

Determination of the Tannin[2] of Hops.—A. C. Chapman.[3] For this purpose a saturated aqueous solution of cinchonine is used, this having been found to be preferable to quinine and strychnine, the hop-tannin being immediately precipitated as a yellow flocculent compound only slightly soluble in water, and practically insoluble in cinchonine sulphate solution. Experiments with pure gallotannic acid ($C_{14}H_{10}O_9$, $2H_2O$) showed that 0·1 gm. gave 0·146 gm. of the cinchonine compound, corresponding to 63 per cent. of gallotannic acid. The compound of hop-tannin contained 4 per cent. of nitrogen (= 42 per cent. of cinchonine), and 58 per cent. of tannin, and was thus similar in composition to the gallotannic acid compound. For calculation 60 per cent. of hop-tannin in the dry alkaloidal precipitate is taken.

PROCEDURE: 10 gm. of hops are placed in a flask marked at 508 c.c., 400 c.c. of boiling water added, and the flask immersed in a boiling water-bath for 2 hours, the hops being macerated from time to time with a glass rod. The flask is cooled to 15°, and made up to the mark with water. The liquid is filtered, and 50 c.c. of the filtrate evaporated to about 15 c.c., and, when cool, 50 c.c. of a saturated aqueous solution of cinchonine sulphate are added, the liquid set aside for 1 to 2 hours in a cool place, and then filtered through asbestos in a Gooch crucible. The precipitate is washed several times with a dilute cinchonine sulphate solution, made by mixing equal volumes of the saturated solution and water, and then dried to constant weight at 100° C. The Gooch crucible before weighing should be treated with a little of this washing solution, and dried at 100° C.

---

[1] From Allen's *Commercial Organic Analysis*, v., 88 (1911).

[2] Lupulo tannic Acid $C_{24}H_{24}O_{13}$.

[3] See *Analyst*, 1908, **33**, 95.

The weight of cinchonine compound, multiplied by 0·6, gives the amount of hop tannin in 1 gm. of the sample.

Kent hops gave amounts of tannin ranging from 2·0 to 2·34 per cent., Worcester hops gave 2·10 per cent. (one sample). Foreign hops examined gave from 2·88 to 4·14 per cent.

Dreaper's Copper Process for Tannic and Gallic Acids.—This is described in a paper contributed to *J. S. C. I.*, 1893, **12**, 412, from which the following abstract is taken.

The methods hitherto proposed for the determination of tannin may be divided into two classes, viz. :—

(1) Those which act by precipitating the tannic acid as an insoluble compound.

(2) Those which act by oxidation.

To the former class belongs the well-known hide-powder process, and to the latter Löwenthal's permanganate method, which has been modified by Procter and others. These fairly represent the two classes, and are the only ones in general use at the present day.

Dreaper, however, has adopted a modified form of Darton's[1] method, the novelty of which consists in precipitating the tannic acid by means of an ammonio-copper sulphate solution, after a preliminary treatment with sulphuric acid to remove the ellagic acid, and then a treatment with ammonia, filtering after each treatment. Procter states that this preliminary treatment is unnecessary in the case of some extracts, but Dreaper has never found any precipitation to take place in the case of the so-called pure tannic acids, probably owing to the removal of the impurities during the process of purification. The original solution and the filtrate are titrated with permanganate as in Löwenthal's method, the difference in the two results being due to the tannic acid present. The copper compound may be dried at 110° C. and weighed, or else ignited and weighed as copper oxide. Fleck states that the tannic acid can be calculated from this by multiplying by the factor 1·034.

The standard copper solution used by the author contained 30 gm. of pure crystallized copper sulphate in a litre of water. Barium carbonate is also required, which should be free from calcium salts.

The process is based on the direct precipitation of the gallic and tannic acids by means of a copper salt, using as outside indicator potassium ferrocyanide. If a standard solution of copper sulphate be run into a solution of the mixed acids, a certain amount of copper tannate and gallate will be precipitated, depending on the dilution of the solution and the amount of acid set free from the copper sulphate The precipitate is, in these circumstances, of a bulky nature and ill adapted to any separation by quick filtration, so necessary in a process of this description. It was found that when a solution of copper sulphate was added to a solution of the mixed acids in the presence of barium carbonate, the precipitation proceeds with the utmost regularity. The carbonate immediately forms insoluble sulphate with the free acid, and also helps to consolidate the precipitated copper salts, so that towards the end of the reaction they fall rapidly to the bottom of the vessel, leaving the supernatant liquid clear. This separation is a good indication that the end of the titration is near, and is supplemented by the ferrocyanide test.

---

[1] *J. Amer. C. S.*, 1882, **4**, 4.

A modified method of testing for the excess of copper in the solution is as follows: Pieces of stout Swedish filter paper one inch square are folded across the middle, and a drop of the liquid to be tested taken up on a glass rod and gently dropped on to the top surface. The liquid will percolate through to the under fold, leaving the precipitate on the upper one. It is then only necessary to unfold the sheet and apply a drop of ferrocyanide to the under surface. If the reaction is complete a faint pink coloration will take place, which is perhaps more easily recognized by transmitted light.

The results obtained by duplicate experiments tend to show that the copper salts are perfectly constant in composition when precipitated in this manner, and the results equal in accuracy any obtained with other processes.

About 1 gm. of barium carbonate was added in each case and the solution heated up to 90° C. before titration. The temperature at the end of the titration should not be less than 30° C.

The precipitation by copper is done on say 25 c.c. of the solution of the sample and the results noted. 50 c.c. of the same sample are then mixed with the usual proportions of gelatine, salt, acid, and barium sulphate, diluted to 100 c.c., then filtered through a dry filter and 50 c.c. (= 25 c.c. of the original liquid) titrated with copper solution as before, the difference being calculated to available tannin.

The experiments show that the separation of the tannic acid by means of an acid solution of gelatine and salt will not affect the general results obtained, and this method for want of a better was used in the experiments, Procter's modification being considered the most accurate, and therefore adopted.

The following table was prepared from experiments, showing the error due to the indicator in c.c. of standard solution added to different quantities of water:—

c.c. of Water.	c.c. of Standard Solution required
20	0·3
30	0·4
60	0·7
100	1·0
150	1·5

The above correction should be made in all cases.

A sample of so-called pure tannic acid gave the following results:—

Weight taken	c.c. required.
Gm.	
0·5	25·0
0·5	25·2
0·5	25·2

Slightly lower results were obtained when the operation was conducted in the old, probably owing to she slower action of the carbonate on the free acid; but he rate of running in of the solution had no appreciable effect on the quantity equired.

A sample of the purest gallic acid that could be obtained gave the following figures :—

Weight taken.	c.c. required.
Gm.	
0·5	45·0
0·5	44·8

Allowing that the acid was of 90 per cent. purity, these results would give a value for each c.c. of 0·0111 gm. This figure must of course only be taken as approximate. It will be seen that more solution is required to precipitate the gallic than the tannic acid. This is also noticed in Lowenthal's method.

Dreaper's latest details[1] for his process are briefly as follows :—

Standard Solutions.—(1) Copper sulphate equivalent to 0·05 CuO per c.c. (157 gm. of the crystallized salt in 1 litre); (2) 20 gm. lead acetate and 60 c.c. glacial acetic acid per litre ; (3) 50 gm. ammonium carbonate and 50 gm. sodium sulphite per litre (the sodium sulphite is used to prevent oxidation during the precipitation).

(*a*) 50 c.c. of the tannin solution (containing 10 to 15 gm. per litre) are titrated with the copper solution after heating to 80° to 90° for a few minutes with excess of $CaCO_3$ (about 1 to 2 gm.) and cooling. The result in terms of CuO represents the total tannin and gallic acid, and any "non-tannins" which precipitate copper salts, but not the non-tannins which may be carried down mechanically.

(*b*) A second 50 c.c. is taken, and 10 c.c. of the lead solution added in the presence of barium sulphate. It is well shaken, and after 5 minutes the lead tannin precipitate is filtered off through dry filter-paper, 0·5 gm. of anhydrous sodium sulphate is added, and after 5 minutes the lead sulphate is filtered off. 40 c.c. of the filtrate is taken and titrated as in (*a*). The result gives the non-tannins precipitated by copper salts (gallic acid), and when subtracted from (*a*) gives the tannins also.

(*c*) To 50 c.c. of tannin solution 25 c.c. of solution (3) above are added. The copper tannate formed on titrating this solution in the cold is free from gallic acid, but only the tannic acids insoluble in ammonium carbonate are precipitated, so that a comparison with the results obtained in (*b*) indicates the amounts of total tannic acid, the two groups of tannic acids, and gallic acid and the non-tannins which may form compounds with copper, respectively. It is generally sufficient in practice to use only the lead separation which entirely removes all tannins, but no gallic acid.

When testing the (*c*) solution for excess of copper by means of a doubled sheet of filter-paper, the ferrocyanide must be strongly acid with acetic acid, and the final result must be confirmed after an interval of 3 minutes, as the copper salt is precipitated slowly in this case.

The process gives the mordant value of any tannin, and is not affected by any "non-tannins" or colouring matter carried down mechanically, or by free acid in the liquors. The presence of reducing sugars has no influence on the results.

---

[1] *C. N.*, 1904, **90**, 111.

The precipitate is ignited, moistened with nitric acid, and re-ignited, and the CuO weighed :

$$CuO \times 1{\cdot}034 = \text{tannic acid.}$$

(This factor probably applies only to gallotannic acid.)

The chief advantage claimed by the author of this method over Lowenthal's are as follows :—

(1) Both the tannic and gallic acids are determined.

(2) Rapidity where a simple assay is sufficient.

(3) The results are expressed in terms of the copper oxide precipitated.

(4) The standard solution keeps well, and there is no correction necessary for indigo solution or gelatine.

(5) Larger quantities of the solution can be titrated, thus reducing the working error.

It seems to be possible to use this method for substances other than tannic or gallic acids, e.g. Fustic.

The following results were obtained with a sample of pure Fustic extract 51° Tw.

0·5 gm. taken required 11·5 c.c. of standard solution.

0·5 gm. taken required 11·6 c.c. of standard solution.

The end of the reaction was sharp when the titration was carried on at the boiling-point and the precipitate settled well.

Other Methods of Determining Tannin.

Direct Precipitation by Gelatine.—The difficulty existing with this method is that of getting the precipitate to settle, so that it may be clearly seen when enough gelatine has been added.

Tolerably good results may sometimes be obtained by using a strong solution of sal ammoniac or chrome alum as an adjunct. The best aid is probably barium sulphate, 2 or 3 gm. of which should be added to each portion of liquid used for titration.

The tannin infusion is diluted with an equal volume of saturated aqueous solution of ammonium chloride, and titrated with a 1 per cent. solution of gelatine in cold saturated ammonium chloride. The end of the action is ascertained by filtering a few drops of the liquid, and testing it with a solution of gelatine on a watch-glass placed on a black surface. Catechu-tannic acid is said to give good results in this way, 1 c.c. of the gelatine reagent representing 0·139 gm. of the tannin.

PART VII.

SPECIAL APPLICATIONS OF THE VOLUMETRIC SYSTEM TO THE ANALYSIS OF URINE.

ANALYSIS OF URINE.

THE complete and accurate determination of the normal and abnormal constituents of urine presents more than ordinary difficulty to even experienced chemists, and is a hopeless task in the hands of any other than such. Fortunately, however, the most important matters, such as urea, glucose, phosphates, sulphates, and chlorides, can all be determined volumetrically with accuracy by ordinary operators, or by medical men who cannot devote much time to practical chemistry. The researches of Liebig, Neubauer, Bence Jones, Vogel, Beale, Hassall, Pavy, Allen, and others, have resulted in a truer knowledge of this important secretion; and to the two first mentioned chemists we are mainly indebted for the simplest and most accurate method of determining its constituents. With the relation which the proportion of these constituents bears to health or disease, the present treatise has nothing to do, its aim being simply to point out the readiest and most useful methods of determining them quantitatively.

One thing, however, is necessary as a preliminary to the examination of urine, which has not generally been sufficiently considered; that is to say, the relation between the quantity of secretion passed in a given time and the amount of solid matters found in it by analysis. From a medical point of view it is a mere waste of time, generally speaking, to determine the constituents in half a pint or so of urine passed at any particular hour of the day or night without ascertaining the relation which that quantity, with its constituents, bears to the whole quantity passed during, say, 24 hours; and this is the more necessary, as the amount of fluid secreted varies very considerably in healthy persons; besides this, the analyst should register the colour, peculiarity of smell (if any), consistence, presence or absence of a deposit (if the former, it should be collected for separate analysis, filtered urine only being used in such cases for examination), and lastly, its reaction to litmus should be observed.

1. Specific Gravity.

This may be taken by measuring 10 c.c. with an accurate pipette into a tared beaker or flask. The observed weight say is 10·265 gm.; therefore 1026·5 will be the specific gravity, water being 1000. Where an accurate balance, pipette, or weights are not at hand, a good urinometer may be used. These instruments are now to be had with enclosed thermometer and of accurate graduation. The specific gravity of normal urine varies from 1015 to 1025.

2. Determination of Chlorides (calculated as Sodium Chloride).

This may be done in various ways. Liebig's method is by far the simplest, but the end point is generally so obscure that the liability to error is very great, and therefore the details of the process are omitted. Mohr's method is modified by the use of ammonium in place of potassium nitrate, owing to the solvent effect which the latter has been found to exert on silver chromate. By ignition the ammonia salt is destroyed.

(*a*) **By Silver Nitrate and Chromate Indicator** (Mohr). 10 c.c. of the urine are measured into a thin porcelain capsule, and 1 gm. of pure ammonium nitrate in powder added; the whole is then evaporated to dryness, and gently charred over an argand burner. The residue is extracted with hot water, passed through a small filter, and washed. The filtrate, which should be colourless, is then ready, after addition of a few drops of potassium chromate, for titration with $N/_{10}$ silver nitrate solution, as on page 147; or for the determination of chlorine by Volhard's method (*b*).

Each c.c. of silver solution represents 0·005846 gm. of salt, consequently if 12·5 c.c. have been used, the weight of salt in the 10 c.c. of urine is 0·073075 gm., and as 10 c.c. only were taken, the weight multiplied by 100, or what amounts to the same thing, the decimal point moved two places to the right, gives 7·3075 gm. of salt for 1000 c.c. of urine.

If 5·9 c.c. of the urine are taken for titration, the number of c.c. of $N/_{10}$ silver used will represent the number of parts of salt in 1000 parts of urine.

(*b*) **By Volhard's Method.**—This is a direct determination of Cl by excess of silver and the excess found by ammonium or potassium thiocyanate (p. 150), which gives very good results in the absence of much organic matter, and is carried out as follows:

10 c.c. of urine are placed in a 100 c.c. flask and diluted to about 60 c.c. 2 c.c. of pure nitric acid and 15 c.c. of standard silver solution (1 c.c. = 0·01 gm. NaCl) are then added; the closed flask is well shaken, and the measure made up to 100 c.c. with distilled water.

The mixture is then passed through a dry filter, and either 70 or 80 c.c. of the clear fluid titrated with standard thiocyanate for the excess of silver, using the ferric indicator described on page 150. The relative strength of the silver and thiocyanate being known, the measure of the former required to combine with the chlorine in the 7 or 8 c.c. of urine is found and calculated into NaCl.

Arnold[1] carries out this process as follows:—

10 c.c. of urine are mixed with 10 to 20 drops of nitric acid sp. gr. 1·2, 2 c.c. of ferric indicator, and 10 to 15 drops of solution of permanganate to oxidize organic matter. The liquid is then filtered and titrated as described above.

---

[1] *Pflüger's Archiv.*, **30**, 541.

3. Determination of Urea.

Carbamide $CO(NH_2)_2$.

If a solution of urea is mingled with an alkaline solution of sodium hypochlorite or hypobromite, the urea is rapidly decomposed and nitrogen evolved, which can be collected and measured in any of the usual forms of gas apparatus described in the section on gas analysis.

$$CO(NH_2)_2 + 3\,NaBrO = 3NaBr + 2H_2O + CO_2 + N_2.$$

Test experiments with pure urea have shown that the whole of the nitrogen contained in it is eliminated in this process, with the exception of a constant deficit of 8 per cent. The carbon dioxide set free in the reaction is absorbed by the excess of caustic alkali present, so that nitrogen gas alone is evolved. In the case of urine there are other nitrogenous constituents present, such as uric acid, hippuric acid, and creatinine, which render up a small proportion of their nitrogen in the process, but the quantity so obtained is insignificant, and may be disregarded. Consequently, for all medical purposes, this method of determining urea in urine is sufficiently exact.

In the case of diabetic urines, however, Méhu and others have pointed out that this deficiency is diminished, and if, in addition to the glucose present, cane-sugar be also added, it will almost entirely disappear. Méhu[1] therefore recommends that in the analysis of saccharine urines cane-sugar be added to the extent of ten times the amount of urea present, when the difference between the actual and theoretical yield of nitrogen will not exceed 1 per cent.

Russell and West[2] have described a very convenient apparatus for working the process, which gives very good results in a short space of time. This method has given rise to endless forms of apparatus devised by various operators, including Méhu, Yvon, Dupré, Apjohn, Maxwell Simpson, Doremus, O'Keefe, etc., etc.; the principles of construction are all, however, the same. Those who may wish to construct simple forms of apparatus from ordinary laboratory appliances, will do well to refer to the arrangements of Dupré[3] or Maxwell Simpson.[4] The nitrometer, with side flask, and using mercury, is perhaps the best of all for the gasometric determination of urea. Each c.c. of N. produced, after correction for temperature, pressure, and moisture, being equal to 0·002913 gm. of urea on the assumption that 92 per cent. is evolved.

The apparatus devised by Russell and West is shown in fig. 53, and may be described as follows:—

The tube for decomposing the urine is about 9 inches long, and about half an inch inside diameter. At 2 inches from its closed end it is narrowed, and an elongated bulb is blown, leaving the orifice at its neck ⅜ of an inch in diameter; the bulb should hold about 12 c.c. The mouth of this tube is fixed into the bottom of a tin tray about 1¾ inch deep, which acts as a pneumatic trough; the tray is supported on legs long enough to allow of a small spirit lamp being held under the bulb tube. The measuring tube for collecting the nitrogen is graduated into cubic centimetres, and is of such size as to fit over the mouth of the decomposing tube; one holding about 40 c.c. is a convenient size. Russell and West have fixed by experiment the proportions, so as to obviate the necessity for correction for pressure and temperature, namely, 37·1 c.c. = 0·1 gm. of urea, since they found that 5 c.c. of a 2 per cent. solution of urea constantly gave 37·1 c.c. of nitrogen at ordinary temperatures and pressures. The entire apparatus can be purchased of most operative chemists for a moderate sum.

---

[1] *Bull. Soc. Chim.* [2], **33**, 410.

[2] *J. C. S.* [2], **12**, 749.

[3] *Ibid.*, 1877, 534.

[4] *Ibid.*, 538.

Hypobromite Solution.—This is best prepared by dissolving 100 gm. of caustic soda in 250 c.c. of water, and at the time required 25 c.c. of the (cold) solution are mixed with 2·5 c.c. of bromine; this mixture gives a rapid and complete decomposition of the urea. Strong solution of sodium or calcium hypochlorite answers equally well.

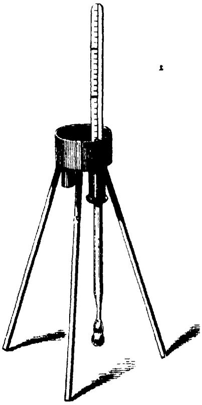
FIG. 53.

METHOD OF PROCEDURE: 5 c.c. of the urine are measured into the bulb-tube, fixed in its proper position, and the sides of the tube washed down with distilled water so that the bulb is filled up to its constriction. A glass rod, having a thin band of india-rubber on its end, is then passed down into the tube so as to plug up the narrow opening of the bulb. The hypobromite solution is then poured into the upper part of the tube until it is full, and the trough is afterwards half filled with water.

The graduated tube is filled with water, the thumb placed on the open end, and the tube is inverted in the trough. The glass rod is then pulled out, and the graduated tube slipped over the mouth of the bulb-tube.

The reaction commences immediately, and a torrent of gas rises into the measuring tube. To prevent any of the gas being forced out by the reaction, the upper part of the bulb-tube is slightly narrowed, so that the gas is directed to the centre of the graduated tube. With the strength of hypobromite solution above described, the reaction is complete in the cold in about 10 or 15 minutes; but in order to expedite it, the bulb is slightly warmed. This causes the mixing to take place more rapidly, and the reaction is then complete in 5 minutes. The reaction will be rapid and complete only when there is considerable excess of the hypobromite present. After the reaction the liquid should still have the characteristic colour of the hypobromite solution.

The amount of constriction in the tube is by no means a matter of indifference, as the rapidity with which the reaction takes place depends upon it. If the liquids mix too quickly, the evolution of the gas is so rapid that loss may occur. On the other hand, if the tube is too much constricted, the reaction takes place too slowly.

The simplest means of supporting the measuring tube is to have the bulb-tube corked into a well, which projects from the bottom of the trough about 1 inch downwards. The graduated tube stands over the bulb-tube, and rests upon the cork in the bottom of the well. It is convenient to have, at the other end of the trough, another well, which will form a support for the measuring tube when not in use.

To avoid all calculations, the measuring tube is so graduated that the amount of gas read off expresses at once what may be called the percentage amount of urea in the urine experimented upon; i.e. the number of grams in 100 c.c., 5 c.c. being the quantity of urine taken in each case. The gas collected is nitrogen saturated with aqueous vapour, and the bulk will obviously be more or less affected by temperature and pressure. Alterations of the barometer produce so small an alteration in the volume of the gas that it may generally be neglected; e.g. if there are 30 c.c. of nitrogen, the quantity preferred, an alteration of 1 inch in the height of barometer would produce an error in the amount of urea of about 0·003; but for more exact experiments, the correction for pressure should be introduced.

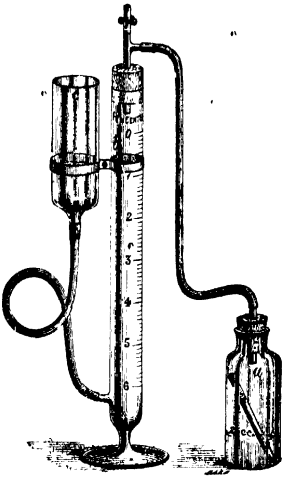

FIG. 51.

In the wards of hospitals, and in rooms where the experiments are most likely to be made, the temperature will not vary much from 65° F., and a fortunate compensation of errors occurs with this form of apparatus in these circumstances. The tension of the aqueous vapour, together with the expansion of the gas at this temperature, almost exactly counterbalances the loss of nitrogen in the reaction.

The authors found from experience that 5 c.c. of urine is the most advantageous quantity to employ, as it usually evolves a convenient bulk of gas to experiment with, i.e. about 30 c.c. They have shown that 5 c.c. of a standard solution containing 2 per cent. of urea evolve 37·1 c.c. of nitrogen, and have consequently taken this as the basis of the graduation of the measuring tube, viz., 37·1 c.c. of the gas as measured represent 0·1 gm. of urea. This bulk of gas is read off at once as 2 per cent. of urea, and in the same way the other graduations on the tube represent percentage amounts of urea.

If the urine experimented with is very rich in urea, so that the 5 c.c. evolve a much larger volume of gas than 30 c.c., then it is best at once to dilute the urine with its own bulk of water; take 5 c.c. of this diluted urine, and multiply the volume of gas obtained by 2.

If the urine contains much albumen, this interferes with the process in so far that it takes a long time for the bubbles of gas to subside before the volume of gas obtained can be accurately read off. It is therefore better in such cases to remove as much as possible of the albumen by heating the urine with 2 or 3 drops of acetic acid, filtering, and then using the filtrate in the usual manner.

Another form of apparatus much used in making this determination is that devised by A. W. Gerrard[1] (fig. 54).

It consists of a graduated tube, which is connected with a second tube, serving as a reservoir, by means of india-rubber tubing. The graduated tube is closed at the top by a rubber stopper, through which passes a T tube, one opening of which is fitted with a short piece of flexible tubing closed by a clip, while the other is connected by a second piece of tubing with a bottle fitted with a perforated cork. In making a test, 25 c.c. of the hypobromite solution are measured into this bottle, then a small test-tube containing 5 c.c. of the urine to be tested is carefully placed in it in such a manner as to avoid contact between the urine and the reagent. The bottle and graduated tube are now connected as shown in the figure, the clip opened, and water poured into the reservoir (*c*) until, by suitably adjusting its height, the water stands at the zero-point in the measuring tube and at the same level in the reservoir—taking care that when this is effected the latter contains but little water.

The clip is then closed, and the bottle so tilted that the urine gradually mixes with the hypobromite solution, the bottle being gently shaken to promote the evolution of gas, which commences immediately and is complete in a few minutes. After 5 (or preferably 10) minutes the reservoir is lowered until the water in it and in the graduated tube stands at exactly the same level, when the volume of gas is read off at once as percentage of urea contained in the urine. If the urine contains more than 3 per cent. of urea, it is necessary to take 2·5 instead of 5 c.c., dilute it with an equal volume of water, and double the result obtained.

4. Determination of Phosphoric Acid (see also pp. 307 et seq.).

The principle of this method is fully described at page 307.

The following solutions are required:—

(1) Standard uranium acetate or nitrate. 1 c.c. = 0·005 gm. P_2O_5 (see p. 308).

(2) Standard phosphoric acid (see p. 309).

(3) Solution of sodium acetate (see p. 308).

(4) Solution of potassium ferrocyanide.—About 1 part to 20 of water, freshly prepared.

Method of Procedure: 50 c.c. of the clear urine are measured into a small beaker, together with 5 c.c. of the solution of sodium acetate (if uranium nitrate is used). The mixture is then warmed in the water-bath, or otherwise, and the uranium solution delivered in from the burette, with constant stirring, so long as a precipitate is seen to form. A small portion of the mixture is then removed with a glass rod and tested as described (p. 309); so long as no brown colour is produced, the addition of uranium may be continued; when the faintest indication of this reaction is seen, the process must be stopped, and the amount of colour observed. If it coincides with the original testing of the uranium solution with a similar quantity of fluid, the result is satisfactory, and the quantity of solution used may be calculated for the total phosphoric acid contained in the 50 c.c. of urine; if the uranium has been used accidentally in too great quantity, 10 or 20 c.c. of the same urine may be added, and the testing concluded more cautiously. Suppose, for example, that the solution has been added in the right proportion, and 19·2 c.c. used, the 50 c.c. will have contained 0·096 gm. phosphoric acid (= 1·92 per 100). With care and some little practice the results are very satisfactory.

---

[1] *Pharm. Journ.* [3], 15, 464.

Earthy Phosphates.—The above determination gives the total amount of phosphoric acid, but it may sometimes be of interest to know how much of it is combined with lime and magnesia. To this end 100 or 200 c.c. of the urine are measured into a beaker, and rendered freely alkaline with ammonia; the vessel is then set aside for 10 or 12 hours, for the precipitate of earthy phosphates to settle; the clear liquid is then decanted through a filter, the precipitate brought upon it and washed with ammoniacal water; a hole is then made in the filter and the precipitate washed through; the paper moistened with a little acetic acid, and washed into the vessel containing the precipitate, which latter is dissolved in acetic acid (some sodium acetate added if uranium nitrate is used), and the mixture diluted to about 50 c.c. and titrated as before described; the quantity of phosphoric acid so found is deducted from the total previously determined, and the remainder gives the quantity existing in combination with alkalis.

5. Determination of Sulphuric Acid.

Standard barium chloride.—A quantity of crystallized barium chloride is to be powdered and dried between folds of blotting-paper. Of this, 30·5 gm. are dissolved in distilled water, and the liquid made up to a litre. 1 c.c. = 0·01 gm. of SO_3.

Solution of sodium sulphate.—1 part to 10 of water.

METHOD OF PROCEDURE: 100 c.c. of the urine are poured into a beaker, a little hydrochloric acid added, and the whole placed on a small sand-bath, to which heat is applied. When the solution boils, the barium chloride is allowed to flow in very gradually as long as the precipitate is seen distinctly to increase. The heat is removed, and the vessel allowed to stand, so that the precipitate may subside. Another drop or two is then added, and so on, until the whole of the SO_3 is precipitated. Much time, however, is saved by using Beale's filter, represented in fig. 23. A little of the fluid is thus filtered clear, poured into a test-tube, and tested with a drop from the burette; this is afterwards returned to the beaker, and more of the test solution added, if necessary. The operation is repeated until the precipitation is complete. In order to be sure that too much of the baryta solution has not been added, a drop of the clear fluid is added to the solution of sodium sulphate placed in a test-tube or upon a small mirror (see p. 339). If no precipitate appears, more barium must be added; if a slight cloudiness takes place, the analysis is finished; but if much precipitate is produced, too large a quantity of the test has been used, and the analysis must be repeated.

For instance, suppose that 18·5 c.c. have been added, and there is still a slight cloudiness produced which no longer increases after the addition of another ½ c.c., we know that between 18½ and 19 c.c. of solution have been required to precipitate the whole of the sulphuric acid present, and that accordingly the 100 c.c. of urine contained between 0·185 and 0·19 gm. of SO_3.

6. Determination of Glucose.

Fehling's method as described on page 412 may be used, but the most suitable methods for urine are Gerrard's cyano-cupric (p. 415), or the Pavy-Fehling.

Process for the Cyano-cupric Solution.—10 c.c. of the clear urine are diluted by means of a measuring flask to 200 c.c. with water, and a large burette filled with the fluid. To 10 c.c. of the cyano-cupric solution prepared as directed (p. 415), are then measured another 10 c.c. of Fehling's copper solution and the liquid brought to boiling; the diluted urine is then delivered cautiously from the burette into the still boiling liquid, and with constant stirring, until the bluish colour has nearly disappeared. The addition of the urine must then be continued more carefully, until the colour is all removed, the burette is then read, and the quantity of sugar in the urine calculated as follows:—

Suppose that 40 c.c. of the diluted urine have been required to reduce the 10 c.c. of copper solution, that quantity will have contained 0·05 gm. of sugar; but, the urine being diluted 20 times, the 40 c.c. represent only 2 c.c. of the original urine; therefore 2 c.c. of it contain 0·05 gm. of glucose, or 25 parts per 1000.

If the Pavy-Fehling solution is used, it is prepared as described on page 413.

Method of Procedure: 10 c.c. of clear urine are diluted as just described, and delivered cautiously from the burette into 50 or 100 c.c. of the Pavy-Fehling liquid (previously heated to boiling) until the colour is discharged. The calculation is the same as before. 100 c.c. of Pavy-Fehling solution = 0·05 gm. glucose.

The ammoniacal fumes are best absorbed by leading an elastic tube from the reduction flask into a beaker of water; the end of the tube should be plugged with a piece of solid glass rod, and a transverse slit made in the elastic tube just above the plug. This valve allows the vapours to escape, but prevents the return of the liquid in case of a vacuum.

7. Determination of Uric Acid.

$C_5H_4N_4O_3$.

A method for the accurate determination of this constituent of urine has, up to the present, not been found; that is to say, although good results may be obtained with chemically prepared pure uric acid, there is no certainty that the same correctness will be attained with the urinary acid as separated in the usual way. The difficulty is caused by the complicated character of the urine itself, and however accurate the process may be with the acid itself in a pure state, it becomes far less reliable when such method is applied to normal or abnormal urine. The precipitation of the acid in combination with some metal, such as silver or copper, carries with it also the so-called alloxuric bases, and the separation by hydrochloric acid contaminates the precipitate with colouring and other matters which militate against its accurate determination with permanganate. I am, however, of the opinion that the latter method is, even now, one of the best for a rapid comparative determination of this constituent.

METHOD OF PROCEDURE: 200 c.c. of the urine are put into an evaporating basin with a few drops of concentrated hydrochloric acid, and evaporated on the water-bath to about half the volume; it is then transferred to a closely-stoppered flask, together with any slight precipitate which may have formed. 5 c.c. of concentrated hydrochloric acid are then added, and the mixture violently shaken for a few minutes. It is then allowed to settle for half an hour, and the liquid passed through a small filter of smooth, hard texture, taking care to pass as little as possible of the sediment on to the filter. About 20 c.c. of cold water are then added to the precipitate in the flask, which is in turn passed through the filter. The filter is then also washed with about the same quantity of water; a hole is then made at its apex, and the small quantity of adhering precipitate washed into the original flask. Finally, about 10 c.c. of concentrated solution of caustic potash (1 : 10) are added to the contents of the flask and slightly warmed until a clear solution is obtained. The mixture is then diluted with about 100 c.c. of cold water, 20 c.c of dilute sulphuric acid added (1 : 5), and the titration with $N/_{10}$ permanganate carried out in the usual manner.

Another form of the permanganate process is to precipitate the phosphates from 100 c.c. of urine with sodium carbonate. The filtrate is mixed with 5 c.c. of a 4 per cent. solution of copper sulphate and 20 c.c. of a solution containing 10 per cent. each of Rochelle salt and sodium thiosulphate. The precipitate so formed is filtered off and well washed with distilled water, then transferred to a flask with about 400 c.c. of water, 5 c.c. of sulphuric acid added, and the uric acid titrated with permanganate.

No absolute weight of uric acid can be calculated from the results, but Mohr assumes that each c.c. of $N/_{10}$ permanganate = 0·0075 gm. of uric acid;[1] the process may, however, be made available for pathological purposes by comparing the results from time to time with the urine from the same person.

The following method has a good claim to accuracy as regards the actual amount of uric acid present in any given specimen of urine, but is tedious. It is based on the fact that an alkaline solution of uric acid reduces Fehling solution in the same way as glucose. The method is worked out by E. Riegler,[2] who found that an average of many experiments gave 0·8 gm. of reduced copper for 1 gm. of uric acid. The acid is first separated from the urine as ammonium urate by Hopkins's method:—

METHOD OF PROCEDURE: 200 c.c. of urine are mixed with 10 c.c. of a saturated solution of sodium carbonate, allowed to stand for half an hour, and filtered from the precipitated phosphates. The precipitate is washed with 50 c.c. of hot water, and to the filtrate and wash-water 20 c.c. of a saturated solution of ammonium chloride added. The liquid is well stirred, and after 5 hours filtered, preferably through a Schleicher and Schüll filter, No. 597, 11 cm. The precipitate of ammonium urate is washed with 50 c.c. of water, and then introduced by means of a jet from a washing-bottle into a 300 c.c. beaker. Several drops of potash are added to clear the liquid, then 60 c.c. of Fehling's solution, and the whole well stirred. The beaker is then heated on wire gauze until the liquid boils, the boiling being continued for 5 minutes. When the precipitate has subsided, the liquid is filtered through a small tough filter (Schleicher and Schüll, No. 590, 9 cm.), the precipitate well washed, and dissolved in 20 c.c. of nitric acid (sp. gr. 1·1), the filter being washed with 60 c.c. of water.

---

[1] This figure has been verified by F. G. Hopkins (Allen's *Chemistry of Urine*, p. 171).

[2] *Z. a. C.*, 1896, 31.

To this solution dry powdered sodium carbonate is added little by little until there is a permanent turbidity. The liquid is then cleared by the cautious addition of dilute sulphuric acid, and made up to 100 c.c. 25 c.c. of this are placed in a 100 c.c. flask, 1 gm. of potassium iodide in 10 c.c. of water added, allowed to stand for 10 minutes, then titrated with standard thiosulphate solution (1 c.c. = 0·002 gm. uric acid), using starch as the indicator. To the total amount of uric acid found in the 200 c.c. of urine, an additional 0·020 gm. should be added to allow for the solubility of the ammonium urate in urine.

The standard thiosulphate solution is made by diluting 126 c.c. of $^N/_{10}$ solution to 500 c.c. The reaction is :—

$$2Cu(NO_3)_2 + 4KI = Cu_2I_2 + 4KNO_3 + I_2.$$

The reduced cuprous oxide may also be weighed directly or reduced to metallic copper, as in the determination of sugar. In the latter case the amount of copper, multiplied by the factor 1·25, gives the corresponding amount of uric acid.

E. H. Bartley[1] points out with reason that the object for which the determination of uric acid is generally made does not require extreme accuracy. The most acceptable process ought to be one which will give consistent results, and which can be quickly accomplished, and though not absolutely exact is nevertheless comparatively so. The method proposed by Bartley is based to some extent upon previous ones by Salkowski, Haycraft, etc., that is to say, the uric acid is precipitated from the urine by silver nitrate in the presence of an excess of ammoniacal magnesia mixture.

Method of Procedure: To 50 or 100 c.c. of the clear urine add 5 c.c. of ordinary magnesia mixture such as is used for phosphates, and about 10 c.c. of ammonia of sp. gr. 0·96,—this must be in excess. Warm the mixture on the water-bath and add from a burette $^N/_{50}$ silver nitrate until a drop of the filtrate, when brought into contact with a drop of weak sodium sulphide solution on a white plate shows a dark ring or cloud. The filtration can be carried out with Beale's filter or a dropping pipette can be used, the end of which is tied over with cotton wool. The clear liquid only must be tested. Each c.c. of silver solution represents 0·00336 gm. of uric acid, and the number of c.c. used (less one half of a c.c. for each 50 c.c. of urine) when multiplied by this factor will give the amount of uric acid in the urine examined. The half c.c. is deducted because it takes that amount of silver solution to give the colour with 50 c.c. of plain water.

---

[1] *J. Am. C. S.*, 1897, 649.

As soon as the process is complete the precipitate settles freely, and it is advisable to test a drop of the clear solution again. The ending can also be checked by adding a drop of the silver to the clear supernatant liquid to see whether a cloudiness appears.

There being no excess of silver in the hot liquid at any time there can be no reduction of the silver. If after the titration is complete the mixture be allowed to cool to ordinary temperature it will be found that 1 to 3 c.c. more silver will be required to give the colour test, and this Bartley attributes to the precipitation of xanthin bases by the silver in a cold solution, which does not take place when the solution is heated.

J. W. Tunnicliffe and O. Rosenheim[1] publish a method which may be rapidly performed when once the uric acid is obtained as ammonium salt by Hopkins's process. The crystals obtained by decomposing the urate with HCl are washed free from the latter on a small filter with repeated small proportions of water to remove all HCl, the uric acid is then rinsed into a flask with 20 or 30 c.c. of hot water, through a hole made in the filter, and is ready for titration

METHOD OF PROCEDURE: This depends on the fact that piperidine combines with uric acid in molecular proportions (4·25 gm. of base equal 8·4 gm. of acid) to form a soluble salt. A $N/_{20}$ solution of the former is prepared by dissolving about 4·2 gm. of piperidine in 1 litre of water, standardizing it on hydrochloric acid of equivalent strength, phenolphthalein being used as indicator. The sample of uric acid separated from ammonium urate as above described is suspended in water, heated nearly to the boiling-point, and the reagent run in; neutrality being shown either by the liquid becoming clear or by the use of phenolphthalein as before. Although the solubility of the urate at 15° is 5·3 per cent., it is better to employ hot solutions; and there is no danger of losing any piperidine by volatilization, as the reaction is instantaneous.

Dr. Edmunds sends me the following remarks as to the determination of uric acid.

1. Chemical uric acid differs entirely in its habitudes from urinary uric acid. Its crystalline form is always uniform as chemical uric acid—colourless—and quite different from urinary uric acid, which, as got from urine, is always coloured yellow-brown, and is protean in its crystalline forms.

2. The problem of titrating chemical uric acid—or pure uric acid—is not quite the same as that of titrating the uric acid in urine. I am not yet able to say in what the difference consists, and I have often crystallized pure uric acid out of iron and other solutions, but have never been able to colour uric acid, nor to get it to crystallize again like urinary uric acid. The only way in which I have succeeded is to add an alkaline solution of chemical urate of potash to a urine out of which I had precipitated all its uric acid with HCl. In that way I found that the uric acid took up from the urine something which gave it the coloration and the protean crystalline form of urinary uric acid. I have thought that urinary uric acid is

---

[1] *Centralbl. Physiol.*, 1897, 11, 434.

really a combination of chemical uric acid with some animal base or coloration of urine.

3. To purify urinary uric acid it should be dissolved (and thrown out by dilution) in H_2SO_4 three successive times. In titrating this with permanganate I am not prepared to give you the reaction, but the practical point is that, as the permanganate goes in by drops, it is instantly decolorized as long as there is any uric acid present, and the end-point is marked quite distinctly (if you are on the look out for it) by a certain hang or hesitation in the decolorization of the permanganate.

4. Fokker's process, as modified by Hopkins, is, I think, the best. The saturation with *pure* NH_4Cl of an acid urine (which should be freshly passed and filtered at 120°) throws out all the uric acid as ammonium urate. This is well set out in Allen's *Chemistry of Urine*, page 168. But much of the work does not say whether the processes have been worked out on the chemical uric acid or on the natural uric acid, freshly obtained from urine. What we have to deal with in medicine is that coloured protean crystalline substance which comes out constantly from urines on adding pure strong HCl and setting aside for 48 hours. That is what we get in the uric acid diathesis, in gout, and in calculi.

For the determination of uric acid I set aside 100 c.c. of fresh urine, filtered at about 120° F., and acidify it with 5 per cent. of pure strong hydrochloric acid. At the end of 48 hours a deposit of uric acid will be seen at the bottom of the tube, and from this a very good idea is gained of the amount of uric acid in the urine. If closer quantification be wanted, the uric acid is collected on a small fine filter paper, washed with a few centimetres of ice-cold distilled water, then dried and weighed, with deduction for the filter paper, and with addition for the uric acid dissolved in the 105 c.c. of acid urinary mother liquor. The amount of uric acid contained in the 105 c.c. of liquid would depend upon the temperature before and at the time of filtration. At 33° F. it would contain only some 2 mgm., at 68° F. it would contain 6 mgm., at 212° F. it would contain 62·5 mgm.

8. Determination of Lime and Magnesia.

METHOD OF PROCEDURE: 100 c.c. of the urine are precipitated with ammonia, the precipitate re-dissolved in acetic acid, and sufficient ammonium oxalate added to precipitate all the lime present as oxalate. The precipitate is allowed to settle in a warm place, then the clear liquid passed through a small filter, the precipitate brought upon it, washed with hot water, the filtrate and washings set aside, then the precipitate, together with the filter, pushed through the funnel into a flask, some sulphuric acid added, the liquid freely diluted, and titrated with permanganate, precisely as on page 180; each c.c. of N/10 permanganate required represents 0·0028 gm. of CaO.

Or the following method may be adopted: -

The precipitate of calcium oxalate, after being washed, is dried, and together with the filter, ignited in a platinum or porcelain crucible, by which means it is converted into a mixture of calcium oxide and carbonate. It is then transferred to a flask by the aid of the washing-bottle, and an excess of N/10 nitric acid delivered in with a pipette. The amount of acid, over and above what is required to saturate the lime, is found by N/10 caustic alkali, each c.c. of acid being equal to 0·0028 gm. of CaO.

In examining urinary sediment or calculi for calcium oxalate, it is first treated with caustic potash to remove uric acid and organic matter, then dissolved in sulphuric acid, freely diluted, and titrated with permanganate; each c.c. of N/10 solution represents 0·0054 gm. of calcium oxalate.

Magnesia.—The filtrate and washings from the precipitate of calcium oxalate are evaporated on the water-bath to a small bulk, then made alkaline with ammonia, sodium phosphate added, and set aside for 8 or 10 hours in a cool place so that the magnesia may separate as ammonio-magnesium phosphate. The supernatant liquid is then passed through a small filter, the precipitate brought upon it, washed with ammoniacal water in the cold, and dissolved in acetic acid, then titrated with uranium solution, as on page 309; each c.c. of solution required represents 0·002815 gm. of magnesia.

9. Ammonia.

The method hitherto applied to the determination of free ammonia and its salts in urine is that of Schlösing, which consists in placing

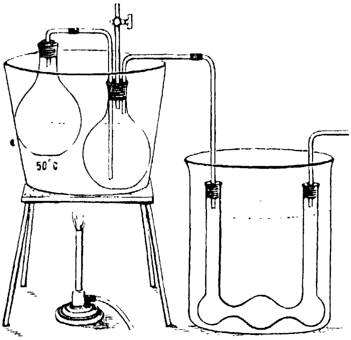

FIG. 55.

a measured quantity of the urine, to which milk of lime is previously added, under an air-tight bell-glass, together with an open vessel containing a measured quantity of standard acid. In the course of from 24 to 36 hours all the ammonia will have passed out of the urine into the acid, which is then titrated with standard alkali to find the amount of ammonia absorbed.

One great objection to this method is the length of time required, since no heating must be allowed, urea evolving free ammonia when heated with alkali. There is also the uncertainty as to the completion of the process; and if the vessel be opened before the absorption is complete, the analysis is spoiled.

Another method which gives good results, and occupies only a short time, has been devised by C. Wurster.[1] The apparatus necessary for it is shown in fig. 55. The principle of the method is the same as Schlösing's, but the liberation of ammonia is hastened by increase of temperature under reduced atmospheric pressure.

---

[1] *Centralblatt. f. Physiologie*, Dec., 1887.

As is well-known, urea is decomposed when urine is boiled with caustic alkali or alkaline earth into ammonium carbonate, but if the operation is carried on at 50° C. and in a partial vacuum, practically no such decomposition occurs. In fact, a solution of artificial urea gives off no ammonia, even when evaporated nearly to dryness with barium, calcium, or magnesium hydrate, in a vacuum at 50° C. Owing to the production of much froth when urine is heated with baryta or lime under reduced pressure, one flask for distillation is not enough, although the frothing may be reduced to some extent by adding some high-boiling hydro-carbon such as paraffin or toluol; but a much safer plan is to use two flasks as shown in the figure, or by using only a small quantity of urine two good-sized boiling tubes will suffice. The boiling-flask dips a small way into the water and the second flask rests on the bottom of the bath; the tube with stop-cock or burette clip, which simply enters below the rubber stopper in this flask, allows air to enter when the operation is ended so as to clear out every trace of ammonia. The absorption tube containing standard acid must have rather long side tubes, and the whole must be immersed in a beaker of cold water. The delivery end of this tube is connected with an efficient water-pump, and of course all connections must be perfectly tight.

Method of Procedure: 10 to 20 c.c. of the urine with 10 to 20 c.c. of saturated barium hydrate or lime solution, with a little water, are placed in the distilling flask, and the water-bath gradually heated up to 50° C., and the whole apparatus is covered with a cloth to avoid regurgitation from cold air. When two-thirds of the distilling liquid have passed over, the ammonia will have all been absorbed by the standard acid, and the valve or stop-cock may be opened while the pump is still working so as to clear away the last traces of vapour.

The method can be used for liquids other than urine.

The following method is available in some cases:—

When a solution containing salts of ammonia is mixed with a measured quantity of free fixed alkali of known strength, and boiled until ammoniacal gas ceases to be evolved, it is found that the resulting liquid has lost so much of the free alkali as corresponds to the ammonia evolved (p. 76); that is to say, the acid which existed in combination with the ammonia in the original liquid has simply changed places, taking so much of the fixed alkali (potash or soda) as is equivalent to the ammonia it has displaced. In the case of urine being treated in this way, the urea will also be decomposed into free ammonia, but happily in such a way as not to interfere with the determination of the original amount of ammoniacal salts. The decomposition is such that, while free ammonia is evolved from the splitting up of the urea, carbonate of fixed alkali (say potash) is formed in the boiling liquid, and, as this reacts as alkaline as though it were free potash, it does not interfere in the slightest degree with the determination of the original ammonia.

Method of Procedure: 100 c.c. of the urine are exactly neutralized with $^{N}/_{10}$ soda or potash, as for the determination of free acid; it is then put into a flask capable of holding five or six times the quantity; 10 c.c. of normal alkali added, and the whole brought to boiling, taking care that the abundant froth which is at first formed does not come over. After a few minutes this subsides, and the boiling proceeds quietly. When all ammoniacal fumes are dissipated, the lamp is removed, and the flask allowed to cool slightly; the contents then emptied into a beaker, and normal nitric acid delivered in from the burette with constant stirring, until a fine glass rod or small feather dipped in the mixture and brought in contact with violet-coloured litmus paper produces neither a blue nor a red spot. The number of c.c. of normal acid are deducted from the 10 c.c. of alkali, and the rest calculated as ammonia., 1 c.c. of normal alkali = 0·017 gm. of ammonia.

It must be borne in mind that the plan just described is not applicable to urine which has already suffered decomposition by age or other circumstances so as to contain ammonium carbonate; in this case it would be preferable to adopt the Wurster or Schlösing method.

10. Determination of Free Acid.

The acidity of normal urine is doubtless due to various substances, among the most prominent of which appear to be acid sodium phosphate (NaH_2PO_4) and lactic acid. Other free organic acids are probably in many cases present. In these circumstances, the degree of acidity cannot be placed to the account of any particular body; nevertheless, it is frequently desirable to ascertain its amount, which is best done as follows:—

100 c.c. of urine are measured into a beaker, and $N/_{50}$ alkali delivered in from a small burette, until a thin glass rod or feather, moistened with the mixture and streaked across some well-prepared violet litmus paper, produces no change of colour; the degree of acidity is then registered as being equal to the quantity of alkali used.

Accurate results are obtained by the method of Gautier, in which the urine is made alkaline by standard caustic soda in known quantity, and the phosphates and other salts precipitated by neutral barium chloride. The liquid is made up to a definite volume with distilled water, and when settled an aliquot portion is titrated with standard acid and phenolphthalein.

11. Determination of Albumen.

The accurate determination of this substance is difficult and troublesome. The best process is perhaps that recommended by Mehu.

Method of Procedure: 100 c.c. of the urine are slightly acidified with acetic acid, 2 c.c. of strong nitric acid are added and the mixture thoroughly agitated. 10 c.c. of a mixture of crystallized carbolic acid 1 part, acetic acid 1 part, and alcohol 2 parts are then added, and the whole well stirred for a few minutes. The precipitate is collected on a small filter and washed with a cold aqueous solution of 4 per cent. of carbolic acid; when fully washed the filter is dried, and together with the paper the precipitate is treated by the Kjeldahl process, and the nitrogen obtained is multiplied by 6·3 for albumen. The presence of sugar or much saline matter does not affect the accuracy of results.

12. Determination of Soda and Potash.

50 c.c. of urine are mixed with the same quantity of baryta solution, allowed to stand a short time, and filtered; then 80 c.c. (= 40 c.c. urine) measured into a platinum dish and evaporated to dryness in the water-bath; the residue is then ignited to destroy all organic matter, and when cold dissolved in a small quantity of hot water, ammonium carbonate added so long as a precipitate is produced, filtered through a small filter, the precipitate washed, the filtrate acidified with hydrochloric acid and evaporated to dryness, then cautiously heated to expel all ammoniacal salts. The residue is then treated with a little water and a few drops each of ammonia and ammonium carbonate, filtered, the filter thoroughly washed, the filtrate and washings received into a tared platinum dish, then evaporated to dryness, ignited, cooled, and weighed.

By this means the total amount of mixed sodium and potassium chlorides is obtained. The proportion of each is found by titrating for the chlorine as on page 147, and calculating as directed on page 150, or the soda may be determined direct by Fenton's method (p. 65).

13. Determination of Total Nitrogen.

This can now be easily accomplished by Kjeldahl's method (p. 85) and is especially serviceable, since it has been found that the results of the titration method for urea by Liebig's process, either in its original way or by subsequent modifications, cannot give the true data for calculating the total nitrogen in any given specimen of urine.

Method of Procedure: 5 c.c. of urine of average concentration are measured into a flask holding about 300 c.c., together with 10 c.c. of sulphuric acid, then gradually heated to boiling, and the heat continued until all vapour and gases are given off and the fluid possesses a clear yellow tint. 25 to 30 minutes generally suffice unless sugar is present in tolerable quantity, in which case mercuric oxide and potassium sulphate must be used, and perhaps more sulphuric acid. The flask is then suffered to cool, the liquid diluted, and distilled with caustic soda and zinc as described on page 89.

PART VIII.

ANALYSIS OF NATURAL WATERS AND SEWAGE.

THE analysis of natural waters and sewage has from an early period received the attention of chemists, but for long no methods of examination were produced which could be said to satisfy the demands of those interested in the subject from various points of view. The researches of Frankland and Armstrong, Miller, Wanklyn, Tidy, Crookes, Dewar, Thresh, and others, have, however, now brought the whole subject into a more satisfactory form, so that it may fairly be said that, as regards accuracy of chemical processes or interpretation of results from a chemical and sanitary point of view, very little addition is required. Considerable space will be devoted to the matter here; and as most of the processes are now volumetric, and admit of ready and accurate results, the general subject naturally falls within the scope of this work. Care has been taken to render the treatment of the matter practical and trustworthy.

The bacteriological examination of waters has now been largely developed and undoubtedly is of the greatest importance, especially with the filtered waters derived from rivers, lakes, and other sources liable to be contaminated with unoxidized surface or drainage impurities. This book has, however, nothing to describe but chemical methods, and therefore no further mention of bacterial investigation will be made.

THE ANALYTICAL PROCESSES.

THE various determinations, etc., required in the analysis of samples of water, sewage, and sewage effluents will be dealt with in the following order:—

1. Collection of samples (p. 445).
2. Preliminary observations (p. 446).
3. Microscopical examination of deposit (p. 446).
4. The determination of total solids (p. 447).
5. ,, ,, suspended matter (p. 448).
6. ,, ,, chlorine (p. 449).
,, ,, nitrogen as nitrates and nitrites:—
7. (i) by Crum's method (p. 449).
8. (ii) by the aluminium method (p. 451).
9. (iii) by the copper-zinc couple (p. 452).
10. (iv) by the phenol-sulphonic acid method (p. 454).

The determination of nitrogen as nitrite:—

11. (i) by metaphenylene - diamine (p. 455).
12. (ii) by the Griess-Ilosvay method (p. 456).
13. (iii) by pot. iodide and starch (p. 457).
14. ,, ,, hardness, by soap (p. 457).
15. ,, ,, hardness, by titration (p. 459).
16. ,, ,, permanent hardness (Pfeifer and Wartha) (p. 460).
17. ,, ,, mineral constituents and metals (p. 460).
18. ,, ,, oxygen absorbed (p. 462).
19. ,, ,, free and albuminoid ammonia (p. 465).
20. ,, ,, organic nitrogen (Kjeldahl) (p. 467).

,, ,, dissolved oxygen in waters and sewage effluents:

21. (i) Roscoe and Lunt's method (p. 468).
22. (ii) Thresh's method (p. 475).
23. (iii) Winkler's method (p. 480).
24. Method of recording results (p. 483).
25. Standards for sewage effluents (p. 484).
26. Preparation of reagents (p. 486).
27. Characteristics of waters derived from various geological formations (p. 490).
28. Interpretation of the results of analysis (p. 491).

Table of analyses of various waters (after p. 498).

NOTE.—All tables required in water analysis will be found at the end of the book.

For the determination of organic carbon and nitrogen, see 10th edition p. 446.

1. Collection of Samples.—The points to be considered under this head are, the vessel to be used, the quantity of water required, and the method of ensuring a truly representative sample.

Stoneware bottles should be avoided, as they are apt to affect the hardness of the water, and are more difficult to clean than glass. Stoppered glass bottles should be used if possible; those known as "Winchester Quarts," which hold about two and a half litres each, are very convenient and easy to procure. One of these will contain sufficient for the general analysis of sewage and largely polluted rivers, two for well waters and ordinary rivers and streams, and three for lakes and mountain springs. If a more detailed analysis is required, of course a larger quantity must be taken.

If corks must be used, they should be *new*, and well washed with the water at the time of collection.

In collecting from a well, river, or tank, plunge the bottle itself, if possible, below the surface; but if an intermediate vessel must be used, see that it is thoroughly clean and well rinsed with the water. Avoid the surface water and also any deposit at the bottom.

If the sample is taken from a pump or tap, take care to let the water which has been standing in the pump or pipe run off before collecting, then allow the stream to flow directly into the bottle. If it is to represent a town water-supply, take it from the service pipe communicating directly with the street main, and not from a cistern.

In every case, first fill the bottle *completely* with the water, thus expelling all gases and vapours, empty it again, rinse once or twice carefully with water, and then fill it nearly to the stopper, and tie down tightly.

At the time of collection note the source of the sample, whether from a deep or shallow well, a river or spring, and also its local name, so that it may be clearly identified.

If it is from a well, ascertain the nature of the soil, subsoil, and water-bearing stratum; the depth and diameter of the well, its distance from neighbouring cesspools, drains, or other sources of pollution; whether it passes through an impervious stratum before entering the water-bearing stratum, and if so, whether the sides of the well above this are, or are not, water-tight.

If the sample is from a river, ascertain the distance from the source to the point of collection; whether any pollution takes place above that point, and the geological nature of the district through which it flows.

If it is from a spring, take note of the stratum from which it issues.

2. Preliminary Observations. In order to ensure uniformity, the bottle should invariably be well shaken before taking out a portion of the sample for any purpose. The *colour* should be observed through a two-foot tube with plate glass ends half-filled with the sample, placed in a horizontal position, and a well-illuminated white surface observed through it. It is well to compare it with distilled water in a similar vessel. The *taste and odour* are most easily detected when the water is heated to 30° to 35° C.

Before commencing the quantitative analysis it is necessary to decide whether the water shall be filtered or not before analysis. This must depend on the purpose for which the examination is undertaken. As a general rule, it the suspended matter is to be determined, the water should be filtered before the determination of nitrogen as ammonia, and total solid residue; if otherwise it should merely be shaken up. If the suspended matter is *not* determined, the appearance of the water, as to whether it is clear or turbid, should be noted.

Water derived from a newly sunk well, or one which has been rendered turbid by the introduction of innocuous mineral matter from some temporary and exceptional cause, should be filtered, but the suspended matter in such cases need not usually be determined.

3. Microscopical Examination of Deposit. The most convenient plan of collecting the deposit is to place a circular microscopical covering glass at the bottom of a large conical glass holding about 20 oz. The glass should have no spout, and should be ground smooth on the top. After shaking up the sample, this vessel is filled with the water, covered with a plate of ground glass, and set aside to settle. After settling, the supernatant water is drawn off by a fine siphon, and the glass bearing the deposit lifted out, either by means of a platinum wire (which should have been previously passed under it), or in some other convenient way, and inverted on to an ordinary microscopical slide for examination. It is desirable to examine the deposit first by a $\frac{1}{5}$th and then by a $\frac{1}{8}$th objective. The examination should be made as soon as the water has stood overnight. If the water be allowed to stand longer, organisms peculiar to stagnant water may be developed and mislead the observer. Particular notice should be taken of bacteria, infusoria, ciliata or flagellata, disintegrated fibres of cotton or linen, or epithelial *débris*.

It is particularly desirable to report clearly on this microscopical examination; not merely giving the general fact that organisms were present, but stating as specifically as possible the names or classes of the organisms, so that more data may be obtained for the application of the examination of this deposit to the characters of potable waters.

It is also desirable to examine the residue left on a glass slide by the evaporation of a single drop of the water. This residue is generally most conveniently examined without a covering glass. The special appearances to be noticed are the presence or absence of particles of organic matter, or organized structure, contained in the crystallized forms which may be seen; and also whether any part of the residue left, especially at the edges, is tinted more or less with green, brown, or yellow.

4. Determination of Total Solid Matter.- This is done by evaporating a known quantity of the water to dryness in a weighed platinum dish on the water-bath. When the residue is not required for any subsequent determination, 250 c.c. are generally taken; but when, as is often the case, the residue is to be used for the determination of nitric and nitrous nitrogen by Crum's method, the amounts usually taken are as follows:—For water supplies and river water—500 c.c. and shallow well-waters—250 c.c.

The sample used should be filtered or unfiltered according to the decision made in that respect at the commencement of the analysis.

For sewage and effluents take 100 c.c.

It is desirable to support the platinum dish during evaporation in a glass ring with a flange, shaped like the top of a beaker, the cylindrical part being about 20 mm. deep. This is dropped into the metal ring on the water-bath, and thus lines the metal with glass, and keeps the dish clean. A glass disc with a hole in it to receive the dish is not satisfactory, as drops of water conveying solid matter find their way across the under surface from the metal vessel to the dish, and thus soil it. As soon as the evaporation is complete, the dish with the residue is removed, its outer surface wiped dry with a cloth, and it is dried in a water or steam oven for about 3 hours. It is then removed to a desiccator, allowed to cool, weighed as rapidly as possible, returned to the oven, and weighed at intervals of an hour, until between two successive weighings it has lost less than 0·001 gm.

With respect to the temperature at which the solid matter should be dried previous to weighing, it should be borne in mind that $CaSO_4, 2H_2O$ when dried at 100° leaves the hydrate $2CaSO_4, H_2O$ and a temperature of 200° to 250° is required to expel the remaining water; also that $MgSO_4, 7H_2O$ loses 6 molecules of water at 120° to 130°, the seventh at 200° to 230°. The Committee appointed by the Society of Public Analysts (see *Analyst*, 1881, 6, 137), recommended the drying of solids at 220° F.

(104·4° C.). Dr. Rideal (*Water and its Purification*) recommends 120°. Prof. Stillman (*Engineering Chemistry*) advises 105°. Dr. Fowler (*Sewage Works Analysis*) dries the solids from sewages and effluents at 100° to 110°, and Dr. McGowan at 110°. Some analysts dry solids at 100°. Hence the necessity for analysts always to state on water and sewage certificates the temperature at which the solids have been dried.

If the residue is not wanted for any other purpose, the dish should be gradually heated to redness and note made of any changes that may take place, especially smell, scintillation, slight darkening or blackening, and partial fusion. The ignited residue may be tested for the presence of phosphoric acid.

5. Determination of Suspended Matter.—Filters of Swedish paper, about 110 mm. in diameter, are packed one inside another, about 15 or 20 together, so that water will pass through the whole group, moistened with dilute hydrochloric acid, washed with hot distilled water until the washings cease to contain chlorine, and dried. The ash of the paper is thus reduced by about 60 per cent., and must be determined for each parcel of filter-paper by incinerating 10 filters, and weighing the ash.[1] For use in determining suspended matter, these washed filters must be dried for several hours at 100° C. or a selected higher temperature (see *infra*), and each one then weighed at intervals of an hour until the weight ceases to diminish, or at least until the loss of weight between two consecutive weighings does not exceed 0·0003 gm. It is most convenient to enclose the filter during weighing in a weighing bottle or in two short tubes, fitting closely one into the other. The closed ends of test tubes, 50 mm. long, cut off by leading a crack round with the aid of a pastille or very small gas jet, the sharp edges being afterwards fused at the blow-pipe, answer perfectly. Each pair of tubes should have a distinctive number, which is marked with a diamond on both tubes. In the air bath they should rest in grooves formed by a folded sheet of paper, the tubes being drawn apart, and the filter almost, but not quite, out of the smaller tube. They can then be shut up whilst hot by gently pushing the tubes together, being guided by the grooved paper. They require to remain about 20 minutes in a desiccator to cool before weighing. Filtration will be much accelerated if the filters be ribbed before drying. As a general rule, it will be sufficient to filter a quarter of a litre of a sewage, half a litre of a highly polluted river, and a litre of a less polluted water; but this must be frequently varied to suit individual cases. When all has passed through, the flask should be rinsed out with distilled water, and the rinsings added to the filter. Thus any particles of solid matter left in the flask are secured, and the liquid adhering to the suspended matter and filter is displaced. The filtrate from the washings should not be added to the previous filtrate, which may be employed for determination of total solid matter, chlorine, hardness, etc.

Thus washed, the filter containing the suspended matter is dried at 100° C. Some analysts, however, prefer to dry at 105°, 110°, or even 120°, but in all cases the temperature should be specified. When drying at any temperature above 100°, the filter should be transferred to the same pair of tubes in which it was previously weighed and dried to constant weight. The weight thus obtained, minus that of tubes and filter, gives the weight of the total suspended matter dried at the temperature selected.

---

[1] Ashless filter-papers can also be purchased.

To ascertain the quantity of mineral matter in this, the filter with its contents is incinerated in a platinum crucible, and the total ash thus determined, minus the ash of the filter alone, gives the weight of the mineral suspended matter.

6. Determination of Combined Chlorine.—To 50 c.c. of the water in a porcelain dish or glass flask add two or three drops of solution of potassium chromate (**C.** ii), so as to give it a faint tinge of yellow, and add gradually from a burette standard solution of silver nitrate (**C.** i), until the red silver chromate which forms after each addition of the nitrate ceases to disappear on stirring or shaking. The number of c.c. of silver solution used will give the chlorine present as chloride in parts per 100,000. If this amount be much more than 10, it is advisable to take a smaller quantity of water.

Where great accuracy is desired the determination is repeated, running in the silver solution gradually to within 1 c.c. of the first reading and then drop by drop, using an equal volume of the water similarly tinted with chromate as a control, if desired. It is absolutely necessary that the liquid examined should not be acid, except with carbonic acid, nor more than very slightly alkaline. It must also be colourless, or nearly so These conditions are generally found in waters, but, if not, they may be brought about in most cases by rendering the liquid just alkaline with lime water (free from chlorine), passing carbonic anhydride to saturation, boiling, and filtering. The calcium carbonate has a powerful clarifying action, and the excess of alkali is exactly neutralized by the carbonic anhydride. If this is not successful, the water must be rendered alkaline, evaporated to dryness, and the residue gently heated to destroy organic matter. The chlorides may then be extracted with water, and determined in the ordinary way either gravimetrically or volumetrically.

7. Determination of Nitrogen as Nitrates and Nitrites (Crum's method).—This method is applicable in the presence of very large quantities either of organic matter or of chlorides (e.g. sea water). For waters generally the method is held in high esteem by many chemists. Nitrogen as nitrates and nitrites in water containing excessive quantities of organic matter and chlorides may be determined by Schlösing's method (see p. 291), taking 100 to 500 c.c. of the sample and concentrating to about 50 c.c.

For Crum's process the total solid residue, in a platinum or glass dish, obtained as in (4) may be used. This is repeatedly treated with a very small quantity of hot distilled water, which is brought into thorough contact with the residue by detaching the latter with a small glass rod covered with a piece of india-rubber. The aqueous extracts, which in all should not exceed about 10 c.c., are passed through a small filter and collected in a little beaker. This is then evaporated over a steam-bath until reduced to about 1 c.c.

This concentrated solution is introduced into the glass tube shown in fig. 56, standing in the porcelain mercury trough, filled up to the stop-cock with mercury. (If the nitrometer of Lunge is used in place of Crum's tube, the use of the laboratory tube and gas apparatus is avoided.) The tube is 210 mm. in total length and 15 mm. in internal diameter. By pouring the liquid into the cup at the top, and then cautiously opening the stop-cock, it may be run into the tube without admitting any air. The beaker is rinsed once with a very little hot distilled water, and then two or three times with strong sulphuric acid (**B.** i), the volume of acid being to that of the aqueous solution about as 3 : 2 The total volume of acid and water should be abou' 6 c.c. Should any air by chance be admitted at this stage, it may readily be removed by suction, the lips being applied to the cup. With care there is but little danger of getting acid into the mouth.

In a few cases carbonic anhydride is given off on addition of sulphuric acid, and must be sucked out before proceeding.

Now grasp the tube firmly in the hand, closing the open end by the thumb, which should be first moistened; withdraw it from the trough, incline it at an angle of about 45°, the cup pointing from you, and shake it briskly with a rapid motion in the direction of its length, so as to throw the mercury up towards the stop-cock. After a very little practice there is no danger of the acid finding its way down to the thumb, the mixture of acid and mercury being confined to a comparatively small portion of the tube. In a few seconds some of the mercury becomes very finely divided; and if nitrates be present, in about a minute or less nitric oxide is evolved, exerting a strong pressure on the thumb. Mercury is allowed to escape as the reaction proceeds, by partially, but not wholly, relaxing the pressure of the thumb. A slight excess of pressure should be maintained within the tube to prevent entrance of air during the agitation, which must be continued until no more gas is evolved.

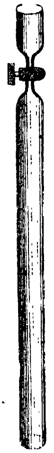

FIG. 56.

When the quantity of nitrate is very large, the mercury, on shaking, breaks up into irregular masses, which adhere to one another as if alloyed with lead or tin, and the whole forms a stiff dark-coloured paste, which it is sometimes very difficult to shake; but nitric oxide is not evolved for a considerable time, then comes off slowly, and afterwards with very great rapidity. To have room for the gas evolved, the operator should endeavour to shake the tube so as to employ as little as possible of the contained mercury in the reaction. At the close of the operation the finely-divided mercury will consist for the most part of minute spheres, the alloyed appearance being entirely gone. An experiment with a large quantity of nitrate may often be saved from loss by firmly resisting the escape of mercury, shaking until it is judged by the appearance of the contents of the tube that the reaction is complete, and then on restoring the tube to the mercury trough, allowing the finely-divided mercury also to escape in part. If the gas evolved be not more than the tube will hold, and there be no odour of nitric peroxide from the escaped finely-divided mercury, the operation may be considered successful. If the amount of nitrate be too large, a smaller quantity of the water must be evaporated and the operation repeated. When no nitrate is present, the mercury usually manifests very little tendency to become divided, that which does so remains bright, and the acid liquid does not become so turbid as in other cases.

The reaction completed, the tube is taken up closed by the thumb, and the gas is decanted into the laboratory vessel, and measured in the usual way in the gas apparatus. The nitric acid tube is of such a length that when the cup is in contact with the end of the mercury trough the open end is just under the centre of the laboratory vessel. If any acid has been expelled from the tube at the close of the shaking operation, the end of the tube and the thumb should be washed with water before introducing into the mercury trough of the gas apparatus, so as to remove any acid which may be adhering, which would destroy the wood of the trough. Before passing the gas into the measuring tube of the gas apparatus, a little mercury should be allowed to run into the laboratory vessel to remove the acid from the entrance to the capillary tube.

As nitric oxide contains half its volume of nitrogen, if half a litre of water has been employed, the volume of nitric oxide obtained will be equal to the volume of *nitrogen* present as nitrates and nitrites in one litre of the water, and the weight of the nitrogen may be calculated in the usual way, with the aid of tables 1 and 2, at the end of this book.

When more than 0·08 part of nitrogen as ammonia is present in 100,000 parts of liquid, there is danger of loss of nitrogen by decomposition of ammonium nitrite on evaporation; and therefore the residue from the determination of total solid matter cannot be used. In such cases acidify a fresh quantity of the liquid with dilute sulphuric acid, add solution of potassium permanganate, a little at a time, until the pink colour remains for about a minute, and render the liquid just alkaline to litmus paper with sodium carbonate. The nitrites present will then be converted into nitrates and may be evaporated without fear of loss. Use as little of each reagent as possible.

Allen[1] advocated the use of Lunge's nitrometer in place of Crum's tube and, to obviate the difficulty in reading the volume of gas which sometimes arises on account of the mercurial froth, he used two nitrometers side by side. In these he worked, under identical conditions, the water-residue and a standard solution of potassium nitrate respectively. A simple calculation then gives the amount of nitrogen required. Allen stated that it is not necessary to make a test experiment each time, as, provided the nitrometer tap is tight, the standard measure of gas obtained from the nitre solution may be kept for an indefinite period. (For list of Nitrogen Conversion Factors, see p. 300).

8. Determination of Nitrogen as Nitrates and Nitrites in Waters containing a very large quantity of Soluble Matter, with but little Ammonia or Organic Nitrogen (The Aluminium Method).—As already stated (see **7**, p. 449) Schlösing's method (p. 291) is applicable for this determination.

In cases where the nitrogenous organic matter present is low the nitrogen as nitrates and nitrites may generally be determined by the following modification of Schulze's method devised by E. T. Chapman. To 200 c.c. of the water add 10 c.c. of sodium hydrate solution (**B.** v), and boil briskly in an open porcelain dish until it is reduced to about 70 c.c. When cold pour the residue into a tall glass cylinder of about 120 c.c. capacity, and rinse the dish with water free from ammonia. Add a piece of aluminium foil of about 15 sq. centim. area, loading it with a piece of clean glass rod to keep it from floating. Close the mouth of the cylinder with a cork, bearing a small tube filled with pumice (**B.** vi), moistened with hydrochloric acid free from ammonia (**B.** vii).

---

[1] *Analyst*, 1880, **5**, 181.

Hydrogen will speedily be given off from the surface of the aluminium, and in 5 or 6 hours the whole of the nitrogen as nitrates and nitrites will be converted into ammonia. Transfer to a small retort the contents of the cylinder, together with the pumice, washing the whole apparatus with a little water free from ammonia. Distil, and determine the ammonia in the usual way with Nessler's solution. It appears impossible wholly to exclude ammonia from the reagents and apparatus, and therefore some blank experiments should be made to ascertain the correction to be applied for this. This correction is very small, and appears to be nearly constant.

9. Determination of Nitrates as Ammonia by the Copper-zinc Couple.—This useful method is founded on the observations of Gladstone and Tribe, the application of the copper-zinc couple to the determination of nitric acid in waters having been suggested by M. W. Williams,[1] who also worked out the practical details of the process. Nitrates are thus reduced, first to nitrites, finally to ammonia, which is then determined.

Preparation of the Copper-zinc Couple.—A piece of clean zinc in the form of foil or very thin sheet, about 3 × 2 inches, is introduced into a bottle and covered with a solution of copper sulphate, containing about 3 per cent. of the crystallized salt. This is allowed to stand—3 or 4 minutes are usually sufficient—till a copious, firmly adherent coating of black copper has been deposited. The solution should then be poured off, and the copper-zinc couple so obtained washed with distilled water, when it is ready for use. The deposition of copper should not be carried too far, or the copper will be so easily detachable that the couple cannot be washed without impairing its activity. The copper solution may be used several times.

METHOD OF PROCEDURE: Place the copper-zinc couple in a wide mouthed stoppered bottle and fill up with distilled water, then pour off and wash with some of the water to be analysed. Then fill the bottle with a further quantity of the water, add a little salt (about 0·1 gm. to every 100 c.c.), insert the stopper and keep the bottle in a warm place for a few hours or overnight. Greater speed, unaccompanied by any loss, is gained by raising the temperature to 30°–38°. Williams proved the value of sodium chloride (also of carbonic acid) in accelerating the reaction, but Dr. G. McGowan[2] states that "The addition of sodium chloride, to accelerate the action of the couple, is absolutely necessary: if it be omitted, the figure obtained for nitrate in a well-nitrated effluent will almost certainly be too low". In the case of calcareous waters, the same hastening effect may be obtained, and the lime at the same time may be removed, by adding a very little pure oxalic acid to the water before digesting it upon the couple. Williams having proved that nitrous acid always remained in the solution until the reduction was complete, the completion of the reaction may be ascertained by testing for traces of nitrous acid. This is done by adding to a portion of the solution 1 c.c. of metaphenylene-diamine reagent (**B.** viii) and acidifying with sulphuric acid. A yellow coloration is produced in about half-an-hour if the least trace of a nitrite is present. When no nitrous acid is found, the water is poured off the couple into a stoppered bottle, and, if turbid, allowed to subside. A measured portion of the clear liquid is then transferred to a Nessler glass, diluted if necessary with ammonia-free water, Nessler's reagent added, and the ammonia present determined in the usual way.

---

[1] *Analyst*, 1881, **6**, 36.

[2] Report on Analysis of Sewage and Sewage Effluents.

This process may be used for the majority of ordinary waters. For those that coloured, and those that contain magnesium or other substances sufficient to interfere with the Nessler reagent, a portion of the fluid poured off the couple should be put into a small retort, and distilled with a little pure lime or sodium carbonate, and the titration of the ammonia performed upon the distillates.

About one square decimetre of zinc should be used for every 200 c.c. of a water containing 5 parts or less of nitric acid in 100,000. A larger proportion should be used with waters richer in nitrates. The couple, after washing, may be used for two or three waters more. When either carbonic or oxalic or any other acid has been added to the water, a larger proportion of Nessler reagent should be employed in titrating it than it is usual to add. 3 c.c. to 100 of the water are sufficient in almost all cases.

Blunt[1] points out that the above process may be used without distillation, and with accuracy, in the case of any water, by adding oxalic acid to a double quantity of the sample, dividing, and using one portion (clarified completely by subsidence in a closely stoppered bottle) as a comparison liquid for testing against the other, which has been treated with the copper-zinc couple. When dilution is used it must be done in both portions equally. This plan possesses the advantages that an equal turbidity is produced by Nessler in both portions, and any traces of ammonia contained in the oxalic acid will have the error due to it corrected.

Prof. P. Frankland[2] carries out the process as follows —

A stoppered bottle (about 200 c.c. capacity) is loosely filled with strips of zinc, which, after cleaning with dilute sulphuric acid, are covered with copper sulphate solution (1 per cent.). The copper-coated strips are repeatedly washed with distilled water, and finally with the water under examination, care being taken not to detach the copper film. The bottle is then completely filled with the sample of water and a crystal of oxalic acid is added, and the bottle, loosely stoppered, is allowed to stand overnight.

A definite volume is withdrawn by means of a pipette, and this is distilled with a suitable volume of ammonia-free water in the ammonia

[1] *Analyst*, 1881, 6, 202.

[2] See Thorpe's *Dict. of Applied Chemistry*, v., 713.

apparatus as usual, a small quantity of ignited sodium carbonate being added. Before withdrawing the water from the bottle for distillation, a small quantity should be tested for nitrite to ensure that the reduction to ammonia is complete. Water containing free or saline ammonia must have this distilled off before being placed in contact with the copper-zinc couple.

Calculation of Results.—In calculating the amount of nitric acid contained in a water from the amount of ammonia obtained in this process, deductions must of course be made for any ammonia pre-existing in the water, as well as for that derived from any nitrous acid present.

Colorimetric Methods for Nitrates and Nitrites.

10. Phenol-Sulphonic Acid Method (Sprengel).—This method is applicable chiefly to waters containing only small proportions of nitrates; nitrites are not affected by it. The solutions required are—

(1) Standard Potassium Nitrate.—Dissolve 0·722 gm. of pure potassium nitrate in a litre of water. Then dilute 50 c.c. of this solution to 500 c.c. with water to make the working standard, of which 10 c.c. are usually taken for each determination

10 c.c. = 0·0001 gm. nitric nitrogen, or 1 part of N in 100,000 of water when 10 c.c. are evaporated.

(2) Phenol-Sulphonic Acid.—Mix together 2 parts by measure of phenol and 5 parts of pure concentrated sulphuric acid, and heat in a porcelain basin on the water-bath for about 6 hours. When cool, add 1½ volumes of water and ½ volume strong hydrochloric acid to each volume of the phenol-sulphonic acid.

Convenient quantities are 80 c.c. phenol, 200 c.c. H_2SO_4; 420 c.c. water and 140 c.c. HCl, producing 840 c.c. of a light brown solution, which is ready for immediate use.

(3) 10 per cent. ammonia (1 vol. ·880 + 2 vols. water); or potash solution, made by dissolving 330 gm. of stick potash (or 236 gm. of caustic soda) in 1 litre of water.

According to Chamot and Pratt the phenol-sulphonic acid contains phenol—2:4—disulphonic acid, together with small quantities of p—phenol-sulphonic acid.

METHOD OF PROCEDURE: 10 c.c. of the water under examination and 10 c.c. of the standard potassium nitrate are pipetted into two small beakers and placed near the edge of a hot plate. When nearly evaporated they are removed to the top of the water-oven and left there till they are evaporated to complete dryness. As this operation usually takes about an hour and a half, it is better, when time is an object, to evaporate to dryness in a platinum dish over steam. The residue in each case is then treated with 1 c.c. of the phenol-sulphonic acid, and the beakers are placed on the top of the water-oven. If the water under examination contain a large quantity of nitrates the liquid speedily assumes a red colour, which, in a good water, will not appear for about 10 minutes. After standing for 15 minutes the beakers are removed, the contents of each washed out successively into a 100 c.c. measuring glass, a slight excess (about 15 c.c.) of 0·96 ammonia or caustic alkali added, the 100 c.c. made up by the addition of water, and the yellow liquid transferred to a

Nessler glass. The more strongly coloured liquid is then partly transferred to the measuring glass again and the tints compared a second time. In this way the tints are adjusted, and when, as far as possible, matched, the liquid that has been partially removed is made up to the 100 c.c. mark with water, and, after well mixing, finally compared. If not exactly the same, a new liquid can at once be made up, probably of exactly the same tint, as the first experiment gives very nearly the number of c.c., of the one equivalent to the 100 c.c. of the other. A. E. Johnson in his very useful *Analyst's Laboratory Companion* (5th ed. p. 92) has given a table for obtaining the nitrogen in parts per 100,000, and also in grains per gallon, by this method.

In the case of very good waters, 20, 50, or more c.c. should be evaporated to a small bulk, rinsed into a small beaker, and evaporated to dryness and treated as above—only 5 c.c. of the standard potassium nitrate (= 0·5 N in 100,000) being taken. In the case of very bad waters, 10 c.c. should be pipetted into a 100 c.c. measuring flask and made up to the mark with distilled water, then 10 c.c. of the well mixed liquid (= 1 c.c. original water) withdrawn and treated as above.

In all cases where the nitric nitrogen exceeds 1·5 parts per 100,000, it is necessary to make a second determination, using such a volume of the water as to give a colour very nearly equal to that of the standard.

This method is inapplicable in the presence of thiocyanates.

It has for a long time been thought that the yellow colour produced as described above was due to the presence of trinitrophenol or picric acid, but Chamot and Pratt[1] have isolated the yellow compound and found it to consist of tripotassium 6--nitrophenol—2: 4—disulphonate NO_2 C_6H_2 $(SO_3K)_2$. OK, 1½H_2O (where potash is added instead of ammonia) They found that picric acid is not formed except in minute traces.

According to A. H. Gill[2] this process does not give the nitrogen present as nitrite, since nitrosophenol C_6H_4 (NO) (OH) is formed and this is colourless in dilute solutions.

This method is not affected by the presence of chlorides.[3]

11. Determination of Nitrites by Griess's Method.—100 c.c. of the water are placed in a Nessler glass, and 1 c.c. each of metaphenylene-diamine $C_6H_4(NH_2)_2$, and dilute acid (**B.** IX) added. If colour is rapidly produced the water must be diluted with distilled water free from N_2O_3, and other trials made. The dilution is sufficient when colour is plainly seen at the end of one minute. The weak point of the process is that the colour is progressively developed; however, this is of little consequence if the comparison with standard nitrite is made under the same conditions of temperature, dilution, and duration of experiment. Twenty minutes is a sufficient time for allowing the colours to develop before final comparison. It is stated that one part of nitrous acid in ten millions of water can easily be detected by this reaction.

M. W. Williams[4] obviates the uncertainty of the comparison tests by using colourless Nessler tubes, 30 mm. wide and 200 mm. long, graduated into millimetres. They are used as follows: A rough comparison of the water to be examined with the standard nitrite is first made; the glasses are then filled to the same height, and the reagent added, and allowed to stand a few minutes. Usually one will be somewhat deeper in colour than the other. The height of the more deeply coloured liquid is read off on the scale, and a portion removed with a pipette, until the colours correspond. The amount of N_2O_3 in the shortened column is taken as equal to the other, when a simple calculation will show the amount sought. Stokes's colorimeter is useful for this purpose.

---

[1] *J. A. C. S.*, 1909, **31**, 922, and 1910, **32**, 630.

[2] *J. S. C. I.*, 1895, **14**, 71.

[3] *Analyst*, 1910, **35**, 81.

[4] *Ibid.*, 1881, **6**, 38.

12. Determination of Nitrites by the Griess-Ilosvay Method.—This method, originally devised by Griess, has been improved by Ilosvay, who introduced the use of acetic acid instead of a mineral acid; the colour so produced is more intense and more rapidly developed. The test depends on the formation of a pink azo-dye by the action of nitrous acid on a mixture of naphthylamine and sulphanilic acid. The following solutions are required.—

(1) ·1 gram of sulphanilic acid ($C_6H_4NH_2SO_3H$) is dissolved, with the aid of heat, in 14·7 gm. of glacial acetic acid mixed with an equal bulk of water. Then more water is added gradually to the warmed liquid, with constant stirring, till 285 c.c. have been used altogether.

(2) 0·2 gm. of α-naphthylamine ($C_{10}H_7NH_2$) is dissolved, with the aid of heat, in 14·7 gm. of glacial acetic acid mixed with twice its bulk of water; then more water is added until 325 c.c. have been used altogether.

These two solutions are kept separately and when mixed in equal volumes form the Griess-Ilosvay solution, which should be made only when required. The latter on keeping tends to become pink, owing to the development of nitrite in the solution from ammonia in the air; it is not affected by light.

This test is almost too delicate to be used quantitatively, but it may be done as follows:—

5 c.c. of standard nitrite solution (1 c.c. = 0·01 mgm. N_2O_3) are mixed with 45 c.c. of pure distilled water in a Nessler glass, and 2 c.c. of the Griess-Ilosvay solution added.

In a similar Nessler glass 50 c.c. of the water to be examined are placed and 2 c.c. of the mixed solutions added.

Both are allowed to stand for 15 minutes before the pink colours are compared. Then the comparison is made as described in the metaphenylene-diamine method (11).

For the determination of nitrous nitrogen in sulphuric acid a standard solution is prepared as follows:—

0·0493 gm. of pure sodium nitrite, which contains 0·01 gm. of N, is dissolved in 100 c.c. of water, and 10 c.c. of this solution is added drop by drop to 90 c.c. of pure sulphuric acid; 1 c.c. of the resulting mixture contains 0·01 mgm. of nitrous nitrogen in a perfectly stable form. Two Nessler glasses are used, and each receives 1 c.c. of the standard solution, 40 c.c. of water, and about 5 gm. of solid sodium acetate. To one of these is added 1 c.c. of the standard solution and to the other 1 c.c. of the acid to be tested, then both are well mixed, and after 10 minutes the colours compared. If they do not correspond, the more strongly coloured liquid is diluted up to the point where the colour corresponds and the percentage of nitrous nitrogen is calculated from the amount of dilution.

13. Determination of Nitrites by Potassium Iodide and Starch.—Ekin[1] has pointed out that this well-known test will give the blue colour with nitrous acid in a few minutes, when the proportion is one part in ten millions; in 12 hours when one part in a hundred millions; and in 48 hours when one in a thousand millions. Experience has proved that waters charged with much organic matter must be clarified by the addition of a little pure alum, then well agitated and filtered before testing.

Ekin used acetic acid for acidifying the water to be tested, and blank experiments with pure water were simultaneously carried on. Sulphuric or hydrochloric acid will, no doubt, give a sharper reaction, but both these acids are more liable to contain impurities affecting the reaction than is the case with pure acetic acid. Owing to the instability of alkali iodides, zinc iodide, which is not open to this objection, is now generally used.

14. Determination of Hardness.—The following[2] method, devised by Dr. Thomas Clark, of Aberdeen, is in general use. It serves to measure more particularly the soap-destroying power of waters and its indications are most useful. The test requires to be carefully performed and should never be done in a hurry, especially in the case of magnesian waters. Both the standardization of the soap solution and the determination of the hardness of a water should be carried out strictly according to the following directions. Before commencing the determination, however, the total solid matter present in a water should be weighed as it gives a useful *approximate* idea of how much to use for the soap test. Although no rule can be given, the total hardness in many waters is about half the total solids, and the sample may be so diluted, if necessary, as to bring it within the limit mentioned below. Thus, if a water contains 50 grains of solids per gallon take 25 c.c. for hardness.

Measure 50 c.c. of the water, or, if necessary, a less quantity (usually 25 or 10 c.c., together with 25 or 40 c.c. of recently boiled and cooled distilled water) into a well-stoppered bottle of about 250 c.c. capacity, shake briskly for a few seconds, and suck the air from the bottle by means of a glass tube, in order to remove any carbon dioxide which may have been liberated from the water. Then run in from a burette standard soap solution (**D** ii), 1 c.c. at a time at first and about 0·3 c.c. towards the end of the operation, shaking vigorously after each addition, until a lather is obtained, which, when the bottle is laid at rest on its side, remains persistent for 5 minutes. Waters containing much magnesium salts give a false lather after the addition of only a few c.c. of soap solution; this, however, disappears entirely on allowing the bottle to remain for several minutes on its side after an extra vigorous shaking. Such waters must always be so diluted that not more than 7 c.c. of the soap solution are required to produce a permanent lather. In other cases the addition of soap solution may be continued until not more than

---

[1] *Pharm. Trans.*, 1881, 286

[2] For the determination of hardness of waters by titration, see p. 459.

16 c.c. are required to produce a permanent lather, which in all cases is attained when, on rolling the bottle half-way round after 5 minutes' standing, the lather still covers the whole surface without breaking. The burette is then read and the hardness ascertained from Table 7, the results being multiplied by 2 or 5 when 25 or 10 c.c. of the water, diluted to 50 c.c., have been used.

It is very important to note that even when the hardness of a water is approximately known, or when making a duplicate determination, the soap solution must always be added a c.c. (or less) at a time, with shaking after each addition, and never in large quantities.

When water containing calcium and magnesium carbonates, held in solution by carbonic acid, is boiled, carbonic anhydride is expelled, and the carbonates precipitated. The hardness due to these is said to be *temporary*, whilst that due to calcium and magnesium sulphates, chlorides, etc., and to the amount of their carbonates soluble in pure water, is called *permanent*.

Water free from carbon dioxide dissolves about 3 parts of calcium carbonate or about 3 parts of magnesium carbonate per 100,000 (but not both simultaneously to this extent), the solubility of both being increased by the chlorides, nitrates and sulphates of the alkalis, and lowered by the carbonates of the alkalis, and by the chlorides. nitrates and sulphates of the alkaline earths. Cavazzi found that the maximum quantity of calcium carbonate dissolved by prolonged agitation (not less than 10 hours) in 1 litre of water saturated with CO_2 and kept in contact with CO_3 at atmospheric pressure is 1·56 gm. of calcium carbonate at 0° C and 1·1752 gm at 15°.

Waters containing sodium carbonate possess no permanent hardness.

To determine *permanent hardness*, a known volume of the water (say 100 c.c.) is boiled gently for half an hour in a flask, the mouth of which is freely open. The level of the water should be marked by an ink or blue pencil mark on the flask, and hot water added from time to time to make up the loss by evaporation. At the end of half an hour, close the flask with a glass marble and cool to ordinary temperature, then make up to the original volume by addition of recently boiled and cooled distilled water, filter through a dry filter, and determine the hardness in the filtrate. The hardness thus found, deducted from that of the unboiled water, will give the *temporary* hardness.

Teed states that calcium salts require 1⅓ and magnesium salts 1½ times the equivalent of soap for the production of a permanent lather. This statement is supported by Helen Masters and H. L. Smith,[1] who used a solution of sodium oleate: they also state that potassium myristate makes a stable soap solution and gives accurate results with calcium and magnesium salts occurring either alone or together. Potassium palmitate solution, they add, deposits an acid soap and is, therefore, unsuitable for this purpose.

According to Prof. H. Jackson :[2] "Every gallon of pure water requires about 10 grains of ordinary soap before a lather can be produced, and each degree of hardness will necessitate the addition of another quantity of 10 grains of soap".

---

[1] *J. C. S.*, 1913, **103**, 992.

Cantor Lectures on Detergents and Bleaching Agents used in Laundry Work, 1907.

In Germany each degree of hardness indicates one part of CaO in 100,000 of water, magnesium salts being reckoned at their equivalent value in CaO.

In France degrees of hardness indicate parts by weight of calcium carbonate in 100,000 parts of water.

Hence 1 English degree = 0·8 German degree
,, ,, = 1·43 French degrees
MgO × 1·39 = CaO.

15. Determination of Hardness by Titration (Hehner's method).—We are indebted, primarily to Mohr, and subsequently to Hehner, for an ingenious method of determining both the temporary and permanent hardness of a water without the use of soap solution.

The standard solutions required are $N/_{50}$ sodium carbonate and $N/_{50}$ sulphuric acid. Each c.c. of standard acid exactly neutralizes 1 mgm of $CaCO_3$ and each c.c. of the alkali precipitates the like amount of $CaCO_3$, or its equivalent in magnesium salts, in any given water.

Method of Procedure: 100 c.c. of the water are tinted with an indicator of suitable character, heated nearly to boiling, and standard acid cautiously added until the proper change of colour occurs. Hehner recommends phenacetolin; but my own experiments give the preference to lacmoid, which is also commended by Thomson. Draper[1] points out the value of lacmoid and carminic acid for such a process, and I fully endorse his opinion with respect to both indicators.

If methyl orange be used, the titration may be made in the cold, this indicator not being affected by CO_2.

If the most accurate results are desired, any of the indicators should be submitted to a blank experiment by taking a measured volume of it with 100 c.c. of distilled water, and finding how much of the acid is required to remove the colour; the quantity of acid so found should then be deducted from all readings before converting them into calcium carbonate.

The number of c.c. of acid used represents the temporary hardness in parts per 100,000. To obtain "degrees of hardness," multiply the number of c.c. by 0·7. The permanent hardness is ascertained by taking 100 c.c. of the water and adding to it a rather large known excess of the standard sodium carbonate. The quantity must of course be regulated by the amount of sulphates, chlorides, or nitrates of calcium and magnesium present in the water; as a rule, a volume equal to that of the water will more than suffice. Evaporate in a platinum dish to dryness (glass or porcelain will not do, as they affect the hardness), then extract the soluble portion with small quantities of distilled water, pass through a very small filter, and titrate the filtrate with the standard acid for the excess of sodium carbonate: the difference represents the permanent hardness.

Some waters contain alkali carbonates, in which case there is of course no permanent hardness, because the salts to which this is due are decomposed by the alkali carbonate. In examining a water of this kind, the temporary hardness will be shown to be greater than it really is, owing to the alkali carbonate; and the experiment for permanent hardness will show more sodium carbonate than was actually added. If the difference so found is deducted from the temporary hardness, at first noted, the remainder will be the true temporary hardness.

---

[1] *C. N.*, **51**, 1885, 206.

16. Determination of Permanent Hardness (Pfeifer and Wartha).—Hehner's method for the determination of permanent hardness is fairly satisfactory when this is due to the presence of lime salts only; but in the frequent cases in which magnesium salts are also present, the modification of Pfeifer and Wartha[1] should be adopted. This is carried out as follows:

200 c.c. of the sample are measured out and transferred to a porcelain dish, 25 c.c. of $\frac{N}{10}$ NaOH and 25 c.c. of $\frac{N}{10}$ sodium carbonate solution are added, and the mixture boiled till the volume is reduced to about 150 c.c. (a 300 c.c. Jena flask may be used instead of a porcelain dish if desired). Cool, transfer to a 200 c.c. measuring flask, and make up to the mark with water. Mix thoroughly, and pour on to a dry filter, rejecting the first 20 c.c. or so (to avoid the interference due to any slight acidity or alkalinity of the filter paper). Pipette 100 c.c. of the filtrate into a beaker and titrate with $\frac{N}{10}$ acid, using methyl orange as indicator. Instead of filtering, the precipitated bases may be allowed to settle and 100 c.c. of the clear supernatant liquid pipetted off. The difference between the number of c.c. of acid required and 25 corresponds to the amount of alkali neutralized by the acids of the salts to which the permanent hardness is due. Hence this number multiplied by (·005 × 1000 ÷) 5 gives permanent hardness in parts per 100,000.

For information on the softening of waters for boiler use see Archbutt and Deeley, *J. S. C. I.*, 1891, **10**, 511, and H R Procter, *ibid.*, 1904, **23**, 8. See also F. A. Anderson, *J. S. C. I.*, 1915, **34**, 1180.

17. Mineral Constituents and Metals.—The quantities of the following substances which may be present in a sample of water are subject to such great variations that no definite directions can be given as to the volume of water to be used. The analyst must judge in each case from a preliminary experiment what will be a convenient quantity to take.

Sulphuric Acid.—Acidify a litre or less of the water with hydrochloric acid, concentrated on the water-bath to about 100 c.c. and while still hot add a slight excess of barium chloride. Filter, wash, ignite, and weigh as barium sulphate, or determine volumetrically, as on p. 336.

Sulphuretted Hydrogen.—Titrate with a standard solution of iodine, as on p. 335.

Phosphoric Acid.—This substance may be determined in the solid residue obtained by evaporation, by moistening it with nitric acid, and again drying to render silica insoluble; the residue is again treated with dilute nitric acid, filtered, molybdic solution added, and set aside for 12 hours in a warm place; filter, dissolve the precipitate in 2½ per cent ammonia, precipitate with magnesia mixture, and weigh as magnesium pyrophosphate, or determine volumetrically as on p. 307 et seq.

---

[1] *Z. a. C.*, 1902, **41**, 198.

Another method is to add to 500 c.c. of the sample about 10 c.c. of solution of alum, then a few drops of ammonia, lastly acidify slightly with acetic acid, and set aside to allow the precipitated $AlPO_4$ to settle. The clear liquid may then be poured off, the precipitate dissolved in nitric acid and determined with molybdic solution.

These determinations are only possible in cases where the P_2O_5 is very large In most waters it is simply necessary to record whether the molybdic precipitate is in heavy or minute traces.

Silicic Acid.—Acidify a litre or more of the water with hydrochloric acid, evaporate to dryness, and dry the residue thoroughly. Then moisten with hydrochloric acid, dilute with hot water, and filter off, wash, ignite, and weigh the separated silica.

Iron.—To the filtrate from the determination of silicic acid add a few drops of nitric acid, dilute to about 100 c.c., and determine by colour titration, as on p. 244; or where the amount is large, add a slight excess of ammonia, and heat gently for a short time. Filter off the precipitate and determine the iron in the washed precipitate colorimetrically.

Calcium.—To the filtrate from the iron determination add excess of ammonium oxalate, filter off the calcium oxalate, ignite and weigh as calcium carbonate or as lime, or determine volumetrically with permanganate as on p 180.

Magnesium.—To the concentrated filtrate from the calcium determination add ammonia, then sodium phosphate (or, if alkalis are to be determined in the filtrate, ammonium phosphate), and allow to stand for 12 hours in a warm place. Filter, ignite the precipitate, and weigh as magnesium pyrophosphate, or, without ignition, titrate with uranium.

Barium.—Is best detected in a water by acidifying with hydrochloric acid, filtering perfectly clear if necessary, then adding a clear solution of calcium sulphate, and setting aside in a warm place. Any white precipitate which forms is due to barium.

Potassium and Sodium.—These are generally determined jointly, and for this purpose the filtrate from the magnesium determination may be used. Evaporate to dryness, and heat gently to expel ammonium salts, remove phosphoric acid with lead acetate, and the excess of lead in the hot solution by ammonia and ammonium carbonate. Filter, evaporate to dryness, heat to expel ammonium salts, and weigh the alkalis as chlorides.

It is, however, generally less trouble to employ a separate portion of water. Add to a litre or less of the water enough pure barium chloride to precipitate the sulphuric acid, boil with pure milk of lime, filter, concentrate, and remove the excess of lime with ammonium carbonate and a little oxalate. Filter, evaporate to dryness, dry at 130° in hot air-oven, and ignite carefully till all ammonia salts are expelled. Dissolve residue in water, transfer solution (filtered, if necessary) to a small weighed platinum dish, evaporate to dryness on water-bath and heat the residue carefully over an Argand Bunsen flame. Cool and weigh KCl + NaCl. If the water contains but little sulphate, the barium chloride may be omitted, and a little ammonium chloride added to the solution of alkali chlorides.

If potassium and sodium must each be determined, separate the potassium by means of platinic chloride; or, after weighing the mixed chlorides, determine the *chlorine* present in them, and calculate the amounts of potassium and sodium by the following formula: Calculate all the chlorine present as potassium chloride; deduct this from the weight of the mixed chlorides, and call the difference *d*. Then as 16·1 : 58·46 : : *d* : NaCl present. (See also p. 150.) Or the sodium chloride may be determined by Fenton's method, p. 65.

Lead and Copper.—Determine by colour titration (Winkler's method) as on p. 256.

Manganese.—Determine colorimetrically, see p. 269.

Arsenic.—Add to half a litre or more of the water enough sodium hydrate, free from arsenic, to render it slightly alkaline, evaporate to dryness, and extract with a little concentrated hydrochloric acid. Introduce this solution into the generating flask of a small Marsh's apparatus, and pass the evolved hydrogen, first through a U-tube filled with pumice, moistened with lead acetate, and then through a piece of hard glass tube about 150 mm. in length, and 3 mm. in diameter (made by drawing out combustion tube). At about its middle, this tube is heated to redness for a length of about 20 mm. by the flame of a small Bunsen burner, and here the arseniuretted hydrogen is decomposed, arsenic being deposited as a mirror on the cold part of the tube. The mirror obtained after the gas has passed slowly for an hour is compared with a series of standard mirrors obtained in a similar way from known quantities of arsenic. Care must be taken to ascertain in each experiment that the hydrochloric acid, zinc, and whole apparatus are free from arsenic, by passing the hydrogen slowly through the heated tube before introducing the solution to be tested. The best form of apparatus (Marsh-Berzelius) is that which is now used for detecting and determining small quantities of arsenic in beer, malt, etc. An electrolytic form of apparatus is also used.

Zinc.—This metal usually exists in waters as bicarbonate, and on exposure of such waters in open vessels a film of zinc carbonate forms on the surface. Potassium ferrocyanide produces a turbidity in such waters owing to the insolubility of zinc ferrocyanide. The reagent will detect 1 part of zinc in 2,000,000 of water. For determination of small amounts of the metal in water, see Winkler, *Z, angew. C.*, 1913, **26**, 38, and p. 256 *supra*.

THE EXAMINATION OF WATER, SEWAGE AND SEWAGE EFFLUENTS FOR ORGANIC IMPURITY.

18. The Determination of the Amount of Oxygen Absorbed from Permanganate.

For the Preparation of the Reagents required, see p. 490.

THIS process, which is sometimes called the oxygen process, was originated by Forchammer and improved by Letheby and by

Tidy. It determines the amount of oxygen taken up in a given time and at a specified temperature in oxidizing the oxidizable organic matter and inorganic salts in a known volume of water slightly acidified with pure sulphuric acid. For this purpose, a standard solution of potassium permanganate is employed in excess. The amount of unchanged permanganate, after a given time, is ascertained by means of a solution of sodium thiosulphate, by the help of the iodine and starch reaction.

Tidy and Frankland in all cases made a blank experiment with pure distilled water side by side with the sample, and this procedure has been adopted generally.

Two tests are usually made, viz., the amount of oxygen absorbed in 3 minutes and in 4 hours respectively. The former, which practically gives the amount absorbed instantaneously, affords a means of differentiating between one class of oxidizable substance and another, and, in the case of sewages and effluents, affords an excellent method, in conjunction with the incubator, of determining the amount of putrefaction which is taking place. In the case of waters, an immediate reduction of permanganate may be caused by such reducing agents as nitrites, ferrous salts, or sulphuretted hydrogen, and Tidy was disposed to attribute this reduction, in the known absence of iron and sulphuretted hydrogen, to nitrites.

The process is carried out as follows:—

The vessels used for this determination should be rinsed with sulphuric acid and then with water. 12-oz. stoppered flasks or 500 c.c. W.M. bottles answer well. First measure out into each flask 10 c.c. of the dilute sulphuric acid, then 10 c.c. of the permanganate, and finally 250 c.c. of distilled water for the blank and the same quantity of each of the samples to be tested. The whole of the vessels are then placed in water at 80° F., or in an incubator, and maintained at that temperature for 4 hours. The flasks should be examined at intervals, and if the pink colour becomes much diminished a further 10 c.c. of permanganate should be added. In all cases a good excess of permanganate should be maintained during the whole of the 4 hours; the flasks should also be shaken occasionally. At the end of 4 hours add to each a few drops of the potassium iodide solution till the clear yellowish-brown colour of iodine replaces the pink of the permanganate. Now run in from a burette the standard solution of thiosulphate with occasional shaking till the colour of the solution is reduced to a pale yellow, then add a few drops of starch solution and more thiosulphate till the blue colour disappears.

Ex. 1. 250 c.c. of water treated as above required 22·4 c.c. thiosulphate; the blank took 32·5 c.c.

$$\cdot 4\left(\frac{32\cdot 5 - 22\cdot 4}{32\cdot 5}\right) = 0\cdot 124 \text{ parts of oxygen absorbed per 100,000 of water.}$$

Ex. 2. Suppose that a sewage effluent required the addition of 30 c.c. of permanganate to maintain a good pink colour, and that 28·1 c.c. of thiosulphate were needed (blank as before), then

$$\cdot 4\left(\frac{32\cdot 5 \times 3 - 28\cdot 1}{32\cdot 5}\right) = 0\cdot 854 \text{ parts of oxygen absorbed per 100,000 of effluent.}$$

To calculate "grains per gallon" instead of "parts per 100,000," use the factor 0·28 instead of 0·4 in the above formulæ

The 3 minutes' test is carried out as follows:—

Ten c.c. of the permanganate solution and the same volume of the dilute sulphuric acid are measured into a small stoppered bottle of about 100 c.c. capacity, and the latter is carefully warmed in a water-bath to the temperature of 80° F. A portion of the sample (sewage, effluent, etc.) is warmed separately to the same temperature, and 25 c.c. of it (or 10 c.c. diluted to 25 c.c. with distilled water, in the case of a very strong sewage) are added to the acid permanganate. The contents of the bottle are mixed by gentle rotation, and after 3 minutes' standing potassium iodide is added and the titration finished as described above. In the case of waters, 250 c.c. are measured into a flask or bottle, such as is used for the 4 hours' test, warmed in a water-bath to 80° F., the acid and permanganate added, etc., as above

Dupré[1] carried out a number of experiments with this process and arrived at the following conclusions:—

(1) That practically no decomposition of permanganate takes place during 4 hours when digested in a closed vessel at 80° with perfectly pure water and the usual proportion of pure sulphuric acid. By adopting the closed vessel, all dust or reducing atmospheric influence is avoided.

(2) The standardizing of the thiosulphate and permanganate, originally and from time to time, must be made in a closed vessel in the same manner as the analysis of a water, since it has been found that when the titration is made slowly in an open beaker less thiosulphate is required than in a stoppered bottle. This is probably due to a trifling loss of iodine by evaporation.

(3) That with very pure waters no practical difference is produced by a rise or fall of temperature, the same results being obtained at 32° F. as at 80° F. On the other hand, with polluted waters, the greater the organic pollution, the greater the difference in the amount of oxygen absorbed according to temperature.

(4) As to time, it appears that very little difference occurs in good waters between 3 and 4 hours' digestion; but with bad waters there is often a very considerable increase in the extra hour; and thus Dupré doubts whether even 4 hours' digestion suffices for very impure waters.

Dupré in further comment on the temperature at which it is advisable to carry out this method (*Analyst* 1885, **10**, 118), and also as to the reactions involved, points out one feature which has in all probability impressed itself upon other operators, that is to say, the effect of chlorides when present in any quantity. It is evident that if in this case the permanganate is used at a high temperature and in open vessels, chlorine will be liberated; part escaping into the air, and the rest nullifying the reducing effect of any organic matter present on the permanganate. If, however, the experiment be conducted at high temperature in a closed vessel, the probable error is eliminated, because the chlorine is retained, and subsequently, when cool and the potassium iodide added, the free Cl liberates exactly the same amount of iodine as would have been set free by the permanganate from which it was produced. It thus becomes possible to determine the amount of oxidizable organic matter, even in sea water. In order, however, to reduce the probable error from the presence of chlorides, Dupré prefers to carry on the experiment at a very low temperature, in fact, as near 0° C. or 32° F. as possible, and uses phosphoric acid in place of sulphuric (250 gm. glacial acid to the litre; 10 c.c. of which is used for each quarter or half litre of water). The sample is cooled, the reagent added in a stoppered bottle, and kept in an ordinary refrigerator for 24 hours. The same operator very rightly condemns the practice adopted by some chemists, especially those of Germany, of boiling a water with permanganate and sulphuric acid. The presence of chlorides in varying proportions must in such case totally vitiate the results.

---

[1] *Analyst*, 1882, 7, 1.

In the interpretation of the results obtained by this process (subject to modification by the other analytical data) the following scale of classification was suggested by Frankland and Tidy:—

	Oxygen Absorbed in 3 hours at Room Temperature from Potassium Permanganate by 100,000 Parts of Water.	
	For Upland Surface Water.	For other Water.
Class I. Water of great organic purity	0—0·1 part	0—0·05 part
„ II. „ medium „	0·1—0·3 „	0·05—0·15 „
„ III. „ doubtful „	0·3—0·4 „	0·15—0·2 „
„ IV. Impure water . . .	above 0·4 „	above 0·2 „

The above must always be used with the greatest caution and in conjunction with the other analytical data as well as with regard to the water's source and history. It should be noted also, that the above table was based on determinations made at room temperature, whereas at the present time such determinations are most commonly made at the temperature of 80° F.

19. Determination of Free and Saline Ammonia and of Albuminoid Ammonia (Wanklyn).

For the preparation of Reagents required, see p. 486.

Measure 500 c.c. of the water to be examined into a stoppered retort or a 32-oz. round-bottomed flask with a rubber stopper, the vessel used being sufficiently large to prevent any of the sample being spurted over into the condenser.[1] Add a small quantity of recently-ignited sodium carbonate and connect by an india-rubber joint with a Liebig's or other condenser, which should be thoroughly rinsed out with good tap-water immediately before use. The distillation should be conducted as rapidly as is compatible with a certainty that no spurting takes place, and a stream of water should be passed through the condenser during the whole of the distillation. When 100 c.c. have distilled over, the receiver (a stoppered 100 c.c. flask) is changed and the distillation continued till another 50 c.c. have been collected in a Nessler glass. The latter is then tested at once with 2 c.c. of Nessler's solution, and if no colour is produced, which is most usually the case, the distillation is stopped. If a colour is produced, further portions are collected and tested till ammonia ceases to come over. In this way the **free and saline ammonia** are obtained.

---

[1] Thorpe's well-known "Revenue Still" is very compact and answers well for water and sewage distillation.

Whilst the distillation has been going on, 50 c.c. of alkaline permanganate and about 25 c.c. of distilled water are together boiled in a nickel dish or a flask for a few minutes to expel any ammonia. If the alkaline permanganate solution, after careful testing, is kept in a place entirely free from ammonia fumes the 50 c.c. can be measured directly into the water without preliminary boiling. This is then poured into the flask and the distillation continued, the distillate being collected in a 100 c.c. flask followed by successive portions in Nessler glasses till the evolution of ammonia has ceased. The ammonia thus collected forms the **albuminoid ammonia.**

The respective distillates are now "Nesslerized" as follows:—Transfer each 100 c.c. distillate to a Nessler glass, add 3 c.c. of Nessler's solution, and mix well with a long glass tube having a bulbed end. The colour that develops enables an approximate estimate to be made of the amount of ammonia present, and one or more standards are made up with ammonium chloride and ammonia-free water as quickly as possible, 3 c.c. of Nessler's solution added to each, and after mixing all are allowed to stand at least 10 minutes, so that the colour may fully develop and all may acquire the room temperature, this latter being a matter of importance The final adjustment is made by pouring some of the more strongly-coloured liquid into a 100 c.c. measuring cylinder until a perfect match of tints is obtained, or a Stokes's Colorimeter may be used. The mode of calculation is best shown by an example.

Ex.: 500 c.c. of water distilled.

Free and saline ammonia. 1st 100 c.c. 85 c.c. gave the same colour as a standard made up of 0·5 c.c. standard NH_4Cl solution (1 c.c. = 0·00005 gm. NH_3). 2nd 50 c.c. None.

Result, $\frac{100}{85} \times 0{\cdot}005 = 1{\cdot}18 \times {\cdot}005$

$= 0{\cdot}0059$ parts free and saline ammonia per 100,000.

Albuminoid ammonia. 1st 100 c.c. was such that 90 c.c. of a standard containing 0·8 c.c. NH_4Cl solution in the 100 c.c. was equal to it in colour. 2nd 50 c.c. none.

Result, $\frac{90}{100} \times {\cdot}008 = 0{\cdot}0072$ parts of albuminoid ammonia per 100,000.

(With 500 c.c. water distilled, 1 c.c. of the standard NH_4Cl solution = 0·01 parts NH_3 per 100,000 of water.)

In the case of **sewages** and **tank effluents** take 50 or 100 c.c. according to strength, add 500 c.c. of pure water, or of good tap water of which the free and albuminoid ammonia are known, then a little Na_2CO_3 and distil till 200 c.c. have been collected in a stoppered flask. Then add 50 c.c. of alkaline permanganate and 100 c.c. of tap-water, also 3 pieces of ignited pumice to prevent bumping and continue the distillation until another 200 c.c. have been collected. Dr. McGowan[1] states that: "In actual practice this distillation is never carried further than the 200 c.c., no matter at what rate the albuminoid ammonia may be coming off when this limit is reached. The estimation is thus only approximate, at least in the case of a sewage or an ordinary effluent. If the distillation of this was carried further (with the addition of successive quantities of ammonia-free water to the retort), albuminoid ammonia would be obtained for an indefinite period in gradually decreasing amounts in the successive fractions of the distillate." Suitable fractions of the distillates are then diluted with ammonia free water to 100 c.c. and Nesslerized. For good filter and land effluents take 250 c.c. and 250 c.c. of tap-water, but if bad 100 c.c. or less and 500 c.c. of tap-water should be used.

20. Determination of Organic Nitrogen in Sewages or Effluents by the Kjeldahl Process.

Dr. McGowan[2] proceeds as follows:—

From 10 c.c. to 100 c.c. of the sample, according to its strength, are boiled down with 4 c.c. of sulphuric acid (free from nitrogen) in a round-bottomed Jena flask, the heating being continued after all the water has been evaporated off, until the acid becomes colourless,—the mouth of the flask being closed by a balloon stopper as soon as the acid begins to fume. When cold, the flask is rinsed out with distilled water into a stoppered measuring flask, a few c.c. of a solution of oxalate of potash (ammonia-free) being sometimes added to throw down the lime present. The solution is then rendered *just* alkaline with purified potash, and filled up to the mark with water. The flocculent precipitate which invariably forms upon the addition of the potash, both in the presence and absence of oxalate, is allowed to subside for at least 24 hours, and a suitable fraction of the clear liquid is then Nesslerized.

A "blank" is made in exactly the same way, substituting distilled water for sewage or effluent. The nitrogen found in the "blank" is then corrected for the minute quantity of nitrogen in the distilled water added before boiling down. The corrected "blank" thus obtained, representing the unoxidized nitrogen in the 4 c.c. of sulphuric acid used, is then subtracted from the corresponding one in the actual determination, the difference giving the organic nitrogen *plus* the nitrogen from the free and saline ammonia present. Finally, by deducting the latter—determined, if possible, by direct Nesslerization of the sample—the organic nitrogen present is obtained. As a rule direct Nesslerization for free and saline ammonia is impracticable, owing to the turbidity produced on adding Nessler's solution. (Dr. McGowan also describes a more elaborate process "with reduction," for details of which the reader is referred to the blue-book already mentioned.)

---

[1] Royal Commission on Sewage Disposal, Vol. IV. Part V. Dr. McGowan's Report on methods of chemical analysis as applied to Sewage and Sewage Effluents, 1904 (p. 14).

[2] Report on Methods of Chemical Analysis of Sewage and Effluents. Vol. IV., Part V of the Fourth Report of the Royal Commission on Sewage Disposal, 1904.

Dr. G. J. Fowler[1] gives the following process:—

30 c.c. of the sample are placed in an 8 oz. flask, a little sodium carbonate added, and it is then distilled with steam till the distillate shows no indication of free ammonia. The steam is generated in a 32 oz. flask and passed into the flask containing the sample. This flask should be heated by a Bunsen burner to prevent the steam condensing in it. In this way the sample is concentrated to about 5 c.c. and is then transferred to an 8 oz. Jena flask with a long neck and 20 c.c. of pure H_2SO_4 (free from Nitrogen) added. The mixture is carefully heated over a naked Bunsen flame in the draught chamber for about half an hour, a little phosphoric anhydride (P_2O_5) is then added, and the heating continued till the mixture is quite clear. After allowing to cool somewhat the mixture is poured into about 200 c.c. of water, and after complete cooling made up exactly to 250 c.c.; 50 c.c. of this solution are then taken, made alkaline with a saturated solution of caustic soda, 500 c.c. of tap-water added, and the ammonia distilled off and Nesslerized in lots of 100 c.c. A "blank" should be made with 35 c.c. of distilled water and all reagents as above, and allowed for. The organic ammonia thus found is always higher than the albuminoid ammonia, and the relation beween the two has been found to vary within fairly wide limits with different samples. In the Fifth Report of the Royal Commission on Sewage Disposal[2] it is stated that "The ratio of albuminoid to total nitrogen in an effluent is usually from 1 : 2 to 1 : 3, though it may in certain cases be either below or above those figures. When an effluent contains a large quantity of suspended solids, the ratio tends to be high."

DETERMINATION OF DISSOLVED OXYGEN.

21. Roscoe and Lunt's Method.

THE volumetric determination of the dissolved oxygen in water is an operation of some importance in water analysis. It is well known that organic and bacterial contamination generally exist side by side; the organic matter offering suitable pabulum for the growth of bacterial life. Water thus contaminated is de-oxygenated by the living organisms which consume oxygen during their growth; hence the importance of the determination of dissolved oxygen in water, as a means of ascertaining the co-existence of the two kinds of impurity.

In brewing also a knowledge of the state of aeration of the wort is sometimes of importance, especially at the fermentation stage of the process.

Several methods have been proposed for carrying out the determination. Mohr's method, depending on the oxidation of ferrous compounds, with subsequent titration by permanganate, has not come greatly into use. Winkler[1] proposed to take advantage of the oxidation of manganous hydroxide (obtained by mixing solutions of a manganous salt and caustic alkali) by dissolved oxygen, the higher oxide formed being decomposed by sulphuric acid and potassium iodide with liberation of iodine, which is determined by titration with sodium thiosulphate. This method is interfered with by the presence of nitrites, which also liberate iodine from acidified potassium iodide; great organic contamination also interferes, inasmuch as the impurities present take up a portion of the liberated iodine.

---

[1] *Sewage Works Analyses*, p. 58.

[2] Cd. 4278, 1908, p. 223.

Schutzenberger's method,[2] fully described in the sixth edition of this book, has received great attention from many operators, some of whom have reported favourably, whilst others find the process unreliable. The reason for the anomalies apparent in the reports of the various experimenters is shown in the results of an interesting and critical investigation of the process carried out by Roscoe and Lunt.[3] They show that an important disturbing influence had been overlooked, and explain many previously ill-understood points in the process.

Schützenberger's original process depends on the reducing action of sodium hyposulphite Na_2SO_2, prepared by the action of zinc dust on a saturated solution of sodium bisulphite containing an excess of sulphurous acid. The determination was originally carried out in a large Woulfe's bottle, of about two litres capacity, filled with pure hydrogen. About 20 to 30 c.c. of water were introduced and slightly coloured blue by indigo-carmine solution. The blue colour was then cautiously discharged by the careful dropping in of hyposulphite solution. To the yellow reduced liquid thus produced, the water to be examined was added from a pear-shaped vessel holding about 250 c.c. The dissolved oxygen restored the blue colour by oxidation, and the amount of hyposulphite required again to decolorize the liquid was noted.

Schützenberger showed that when a small amount of indigo was employed in the determination, the yellow colour produced when the titration was completed quickly returned to blue, and this when decolorized again turned blue, and so on for some time, until double the amount of hyposulphite first added had been used. He showed also that by using a much larger amount of indigo the double portion of hyposulphite was required *at once*.

By titrating an ammoniacal solution of copper sulphate with the hyposulphite used he arrived at a value (though an erroneous one) for the hyposulphite employed in his experiments, and concluded that, at the first yellow colour produced in a titration where a small amount of indigo was used, only *half* the oxygen actually present had been obtained. The other half he accounted for by saying that the reaction between hyposulphite and dissolved oxygen is such that one-half the oxygen becomes latent as hydrogen peroxide, which slowly gives up half its oxygen. He thus accounted for the return of the blue colour, as well as his observation that only ha'f the oxygen was at once obtained. To explain the observation that when a large amount of indigo was employed *the whole* of the dissolved oxygen was found, he assumed that a different reaction takes place, one between dissolved oxygen and reduced indigo, in which the peroxide of hydrogen is not formed.

---

[1] *Berichte*, 1888, **21**, 2851.

[2] See "Fermentation" by P. Schutzenberger (*International Scientific Series*).

[3] *J. C. S.*, 1889, 552.

Ramsay and Williams,[1] whilst agreeing with Schutzenberger and with Dupré,[2] that the process gives reliable results, throw a doubt on the chemical explanation given of the above experiments.

Instead of the ratio 1 : 2, they find 3 : 5 to be the ratio between the first and the total quantity of hyposulphite required when a small amount of indigo is employed, but give it only as the mean expression of the varying ratios they obtain, and add "but it is difficult to devise an equation which will in a rational manner account for this partition of oxygen" into two stages of the process. Roscoe and Lunt's investigation[3] has thrown a new light on these experiments. They show (1) that a series of fifteen determinations carried out with every care in improved apparatus, and under apparently identical conditions, gave discordant results, varying between 4·55 and 6·50 c.c. of hyposulphite for the same volume of water, showing a difference of 0·35 per cent. of the mean value. (2) The rapidity of titration has a great influence on the result. The mean of a series of ten determinations carried out drop by drop was 5·47, whilst ten experiments with the same sample of water gave a mean of 7·12 when the titration was performed quickly. (3) Not only is a low result obtained by a slow titration and a high result by a quick one, but by varying the time of titration still more *extreme* variations in the result are obtained; any value between 1 and 100 per cent. of the total oxygen present being shown to be possible. (4) The ratio between the first reading and the total quantity of hyposulphite required is not a constant one, and is shown to be capable of an infinite range of variation.

The key to the explanation of these remarkable results is given by the authors as follows: "The conclusion" from their experiments "was, that when aerated water is introduced into an atmosphere of pure hydrogen, it immediately begins to lose oxygen by *diffusion* into the hydrogen until an equilibrium is established." By the recognition of this disturbing influence, the previous anomalies are easily explainable on the following data:—

(1) Discordant results are obtained from the same water, because the several titrations are not performed in exactly the same time, therefore, varying amounts of oxygen diffuse, and leave a varying residue for titration.

(2) The high results of a quick titration are accounted for by the fact that a large amount of oxygen is titrated *and fixed* before it has had time to diffuse, whilst the slow titration gives a low result, because a large amount of oxygen has already diffused from the liquid before the titration is completed. No greater proof of the rapidity with which the water under examination lost oxygen by the old process need be given than the fact that Schutzenberger's results show that half the oxygen had left the liquid by diffusion before the determination could be completed.

(3) The return of the blue colour is due to the re-absorption of the

---

[1] *J. C. S.*, 1886, 751. [2] *Analyst*, 1885, 10, 156. [3] *J. C. S.*, 1889, 552.

diffused oxygen by the sensitive yellow liquid, oxidation by gaseous oxygen producing the blue colour, which is thus not due to a reaction within the liquid.

(4) The whole of the oxygen is obtained when a large amount of indigo is used, because when reduced it is capable of *at once* fixing the whole of the dissolved oxygen and thus prevents diffusion. The use of so large a quantity of indigo, necessary to effect this result, however, so disturbs the end-reaction that "it is difficult to fix the point at which the last trace of blue has been discharged with any degree of accuracy"

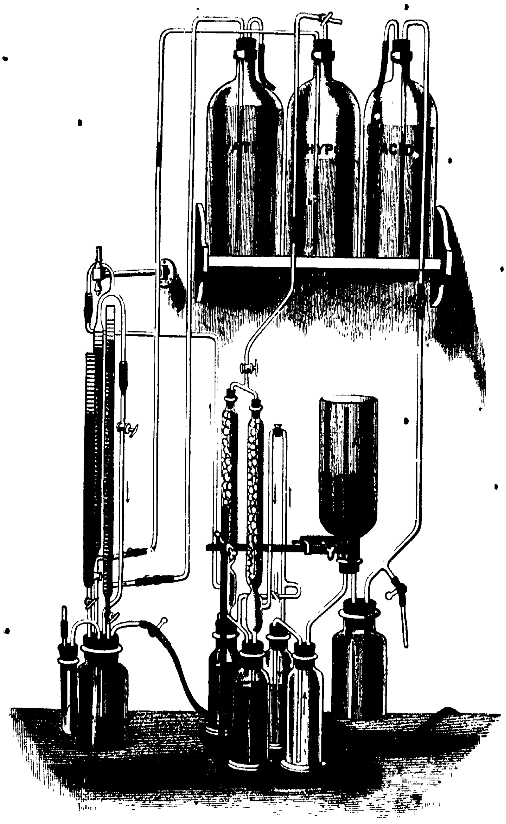

FIG. 57.

(Dupré *loc. cit.*). Hence a new method must be resorted to in which diffusion is eliminated, and Roscoe and Lunt have devised the following method to satisfy the conditions of the case. The apparatus employed by them is shown in fig. 57.

It consists essentially of (1) an apparatus for the continuous generation and purification of hydrogen, by the action of dilute sulphuric acid on zinc; (2) a 200 c.c. wide-mouthed bottle, fitted with three burettes with glass taps, inlet and outlet tubes for a current of hydrogen, and an outlet tube for the titrated liquid; (3) Winchester stock bottles of hyposulphite, indigo (not shown), and water (sample), communicating with their respective burettes by *glass*[1] siphons. The hydrogen generated in A passes through two wash-bottles containing caustic potash, thence through two Emmerling's tubes filled with glass beads, moistened with an alkaline solution of potassium pyrogallate, an arrangement being made whereby the beads may be re-moistened with fresh pyrogallate from the bottles beneath, the liquid being forced up by hydrogen pressure. Pure hydrogen is supplied continuously (1) to the stock bottle of hyposulphite, (2) to the hyposulphite burette, and (3) to the titration bottle.

Preparation of the Reagents.—The reagents required are:—

Hyposulphite solution (Na_2SO_2).

Indigo solution.

Standard aerated distilled water.

The Hyposulphite Solution is prepared by dissolving 125 gm. of sodium bisulphite in 250 c.c. of water, and passing a current of SO_2 through the solution until saturation is effected. The solution is poured into a stoppered bottle of about 500 c.c. capacity, containing 50 gm. of zinc dust, the bottle is almost filled up with water, and the mixture well shaken for 5 minutes, after which the bottle is placed beneath a running tap to cool. The mixture is again agitated after a quarter of an hour and left to deposit the excess of zinc. The clear liquid is poured off from the sediment into a Winchester quart bottle half full of water. Milk of lime is added in excess, and the solution made up to fill the bottle almost completely. The mixture is now thoroughly shaken and allowed to stand (best overnight) until clear.

The solution thus obtained is much too strong for use. 200 c.c. of this may be poured into a Winchester quart bottle of water (never into a bottle filled with air) and well shaken with as little air as possible. The approximate strength of this dilute solution must now be found by titrating good tap water in the apparatus already described. The strength should be such that 100 c.c. of water requires about 5 c.c. of hyposulphite, and the solution should be made up approximately to this value. It slowly loses strength on keeping, even in hydrogen, and its value should be determined daily as required to be used.

The Indigo-carmine solution is really sodium or potassium sulphindigotate, and is prepared by shaking up 200 gm. of this substance in a Winchester quart bottle of water, and filtering the blue solution, which must be diluted to such a strength that 20 c.c. require about 5 c.c. of the above hyposulphite solution for decolorization.

---

[1] India-rubber tubing must not be used for the conveyance of the hyposulphite solution (or the water under examination), as atmospheric oxygen rapidly diffuses through the india-rubber and affects the strength of the solution.

Standard Aerated Distilled Water.—Two Winchester quart bottles half-filled with freshly-distilled water are vigorously agitated for 5 minutes, and the air renewed several times by filling up one bottle with the contents of the other, and again dividing into two portions, which are repeatedly shaken with fresh air. Finally, one bottle being filled, the temperature of the water is taken, and also the barometric pressure, after which the bottle is allowed to stand stoppered for half an hour, to get rid of minute air-bubbles. Table No. 7, due to Roscoe and Lunt, gives the volume of oxygen contained in this standard aerated water, and the results show that Bunsen's coefficients, previously used, are inaccurate.

THE DETERMINATION: The burette having been filled, and a preliminary trial made -

(1) 20 c.c. of the water are introduced into the small bottle and about 3 c.c. of indigo solution added.

(2) A moderate current of hydrogen is passed through the blue liquid by a very fine jet for 3 minutes to free both water and supernatant gas from free oxygen.

(3) Hyposulphite is now carefully added, during the flow of hydrogen, until the change from blue to yellow occurs, taking care not to overstep this point.

(4) A further measured quantity of hyposulphite is now added (say 10 c.c.) sufficient to combine with all the dissolved oxygen in the volume of water (50 to 100 c.c.) proposed to be used in the determination.

(5) The important point is that the water be now quickly run in from a burette by a capillary tube passing *beneath the surface of the liquid* to the bottom of the vessel. The water is thus introduced into a liquid which will *at once* fix the free oxygen and thus prevent its diffusion on coming in contact with the hydrogen, the reduced indigo acting as an indicator for the complete oxidation of the hyposulphite. The liquid is kept in constant motion during the addition of the water, which is shut off the moment a permanent blue colour appears.

(6) The blue is decolorized by a further slight addition of hyposulphite. The volume of water used and the total hyposulphite, minus the first addition, are noted and the determination repeated for confirmation.

When the water contains very little oxygen the second addition of hyposulphite may be omitted, the reduced indigo being sufficient to take up all the dissolved oxygen. In this case, care must be taken that the oxygen added should require not more than half the hyposulphite first added to decolorize the indigo.

Standardizing the Hyposulphite.—In order to complete the determination it is necessary to know the strength of the hyposulphite solution employed, and for this purpose the bottle of standard aerated distilled water is titrated. This method has the great advantage that it is a titration carried out under almost the same conditions as the examination of the sample. The result of a determination is easily obtained by the following formula:—

$$\frac{d \times hs \times Od}{s \times hd} = x \text{ c.c. dissolved Oxygen per litre of water}$$

where d and s = the volumes of distilled water and sample respectively used, hd and hs = the hyposulphite required for the distilled water and sample respectively, and Od the volume of dissolved oxygen contained in one litre of the standard water.

Standardizing the Indigo.—When once the hyposulphite has been carefully standardized by distilled water, the rather troublesome aeration may be avoided by finding the oxygen value of the indigo solution. This solution remaining constant may be used for the subsequent standardizing of the hyposulphite.

It is only necessary to take a suitable quantity of indigo solution, diluted with water if necessary, free it from all dissolved oxygen by a current of pure hydrogen continued for 5 minutes, then carefully decolorize with hyposulphite, the value of which has been found by using aerated distilled water.

The authors show that Schutzenberger's method of standardization, depending on the decolorization of ammoniacal copper sulphate, gives inaccurate results.

Free acids or alkalis greatly disturb the process. Bicarbonates have no effect. Of course when substances other than oxygen, which decompose hyposulphite, are present, the accuracy of the method is proportionately disturbed. The authors have applied the process to waters of very varied character, and containing widely different amounts of oxygen, and show that the method is capable of giving good results, compared with the actual volume of oxygen found by extracting the gases by boiling *in vacuo*.

The delicacy of the reaction is such that one part of oxygen in *two million* parts of water is easily detected.

The following numbers were obtained from five different samples of London tap water collected on five different days:—

	(1)	(2)	(3)	(4)	(5)
	c.c.	c.c.	c.c.	c.c.	c.c.
Nitrogen	13·22	13·95	13·36	13·43	13·49
Oxygen	5·15	5·91	5·38	6·31	5·80
Carbon dioxide . . .	7·98	9·29	6·70	7·35	8·11
Total Gas . . .	26·35	29·15	25·44	27·09	27·40
Oxygen by the new volumetric method . . .	5·52	6·13	5·64	6·41	6·24
Gas obtained . . .	5·15	5·91	5·38	6·31	5·80
Difference . . .	0·37	0·22	0·26	0·10	0·44
Mean difference 0·28 c.c. oxygen per litre of water.					

The oxygen values obtained by the two methods show close agreement, considering the possible experimental error in so complex a comparison.

M. A. Adams[1] describes and figures a very convenient arrangement for carrying out this process, which is well adapted for technical work, and less cumbrous than the apparatus here described.

22. Iodimetric Method.

A simpler method than the foregoing has been proposed by Thresh,[2] which by comparison with Roscoe and Lunt's method appears to give satisfactory results when aerated distilled water was under titration, the differences occurring only in the second decimal place. The author was led to investigate the method by observing the larger amount of iodine which a very minute quantity of a nitrite caused to be liberated when potassium iodide and dilute sulphuric acid were added to water containing it. The amount of iodine liberated varies with the length of exposure to air. If air is excluded no increase of free iodine occurs after the first few minutes, and if the water is previously boiled and cooled in an air-free space still less iodine is liberated. In this latter case the action is represented by the equation—

$$2HI + 2HNO_2 = I_2 + 2H_2O + 2NO.$$

When oxygen has access to the solution, the nitric oxide acts as a carrier, and more hydrogen iodide is decomposed, the nitric oxide apparently remaining unaffected, and capable of causing the decomposition of an unlimited quantity of the iodide.

This reaction is the one utilized in the process devised by Thresh for determining the oxygen dissolved in water. As 16 parts by weight of oxygen will liberate 253·84 parts of iodine, thus—

$$2HI + O = H_2O + I_2,$$

and as the latter element admits of being accurately determined, theoretically the oxygen should be capable of very precise determination. Practically such is the case; the oxygen dissolved in drinking waters admits of being determined both rapidly and with precision. It is only necessary to add to a known volume of the water a known quantity of sodium nitrite, together with excess of potassium iodide and acid, avoiding access of air, and then to determine volumetrically the amount of iodine liberated. After deducting the proportion due to the nitrite used, the remainder represents the oxygen which was dissolved in the water and in the volumetric solution used.

The following are the reagents required :—

(1) Solution of sodium nitrite and potassium iodide :—

Sodium nitrite	0·5 gm.
Potassium iodide	20·0 gm.
Distilled water	100 c.c.

(2) Dilute sulphuric acid :—

Pure sulphuric acid	1 volume
Distilled water	3 volumes

(3) A clear, freshly made solution of starch.

---

[1] *J. C. S.*, 1892, **61**, 310.

[2] *Ibid.*, 1890, **57**, 185.

(4) A volumetric solution of sodium thiosulphate :—
Pure crystals of thiosulphate, 7·75 gm.
Distilled water to 1 litre.
1 c.c. corresponds to 0·25 milligram of oxygen.

The apparatus required is very simple, and can readily be fitted up. It consists of a wide-mouthed white glass bottle (A, fig. 58) of about 500 c.c. capacity, closed with a rubber stopper having four perforations. Through one passes the tube B, drawn out at its lower extremity to a rather fine point, and connected at the upper end, by means of a few inches of rubber tubing, with the burette C, containing the thiosulphate. Through another opening passes the nozzle of a separatory tube D, having a stopper and stopcock. The capacity of this tube when full to the stopper must be accurately determined. Through the third opening passes a tube E, which can be attached to an ordinary gas supply. Through the last aperture is passed another tube, for the gas exit, and to this is attached a sufficient length of rubber tubing to enable the cork G at its end to be placed in the neck of the tube D when the stopper is removed. A small piece of glass tube projects through the cork, to allow of the escaping gas being ignited.

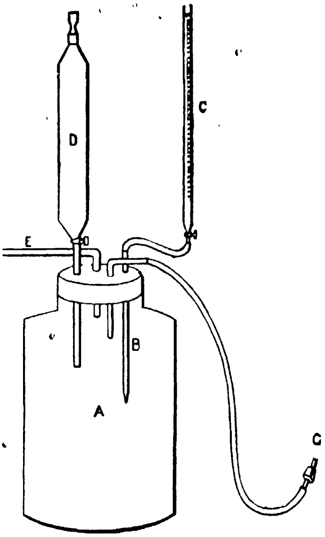

FIG. 58.

The apparatus is used in the following manner: The bottle A being clean and dry, the perforated bung is inserted, the burette charged, and the tube B fixed in its place. E is connected with the gas supply. The tube D is filled to the level of the stopper with the water to be examined, 1 c.c. of the solution of sodium nitrite and potassium iodide added from a 1 c.c. pipette, then 1 c.c. of the dilute acid, and the stopper instantly fixed in its place, displacing a little of the water, and including no air. If the pipette be held in a vertical position with its tip just under the surface of the water, both the saline solution and the acid, being much denser than the water, flow in a sharply defined column to the lower part of the tube, so that an infinitesimally small quantity (if any) is lost in the water which overflows when the stopper is inserted. The tube is next turned upside down for a few seconds for uniform admixture to take place, and then the nozzle is pushed through the bung of the bottle, and the whole allowed to remain at rest for 15 minutes, to enable the reaction to become complete. A rapid current of coal gas is now passed through the bottle A, until all the air is displaced and the gas burns at G with a full luminous flame; the flame is now extinguished, the stopper of D removed, and the cork G rapidly inserted. On turning the stopcock, the water flows into the bottle A. The stopcock is turned off, the cork G removed, and the supply of gas so regulated that a small flame only is produced when this gas is ignited at G. Thiosulphate is now run in until the colour of the iodine is nearly discharged. A little starch solution is then poured into D, and about 1 c.c. allowed to flow into the bottle by turning the stopcock. The titration with thiosulphate is then completed. After the discharge of the blue colour, the latter returns faintly in the course of a few seconds, due to the oxygen dissolved in the volumetric solution; after standing about two minutes, from 0·05 to 0·1 c.c. of thiosulphate must be added to effect the final discharge. The amount of volumetric solution used must now be noted. This will represent *a*, the oxygen dissolved in the water examined, + *b*, the nitrite in the 1 c.c. of solution used, and the oxygen in the acid and starch solution + *c*, a portion of the dissolved oxygen in the volumetric solution. To find the value of *a*, it is obvious that *b* and *c* must be ascertained. This can be effected in many ways, and once known does not require re-determination unless the conditions are changed.

To Find the Value of b.—Probably the best plan is to complete a determination as above described, and then, by means of the stoppered tube, introduce into the bottle in succession 5 c.c. of nitrite solution, dilute acid, and starch solution. After standing a few minutes, titrate. One-fifth of the thiosulphate used will be the value required.

To Find the Value of c.—This correction is a comparatively small one, and admits of determination with sufficient accuracy if it is assumed that the thiosulphate solution normally contains as much dissolved oxygen as distilled water saturated at the same temperature. Complete a determination as above described, then remove the stoppered tube, and insert a tube similar to that attached to the burette, and drop in from it 10 or 20 c.c. of saturated distilled water exactly as the thiosulphate is dropped in. Allow to stand a few minutes and titrate. One-tenth or one-twentieth of the volumetric solution used, according to the number of c.c. of water added, will represent the correction for each c.c. of volumetric solution used. Call this value *d*.

Let *e* be the number of c.c. of thiosulphate used in an actual determination of the amount of oxygen in a sample of water;

f = the capacity in c.c. of the tube employed − 2 c.c., the volume of reagents added;

g = the amount of oxygen in milligrams dissolved in 1 litre of the water;

then $$g = \frac{1000}{4f}(e - b - ed).$$

With a tube made to hold exactly 250 c.c., the most convenient quantity to use, $\frac{1000}{4f}$ becomes unity, and

$$g = e - b - ed.$$

In the author's experiments two nitrite solutions were used; in the first $b = 2{\cdot}1$ c.c., in the second 3·1 c.c. A number of determinations of d were made, at temperatures varying from 40° to 60° F. The value of d was found to vary between 0·03 and 0·0315. In all the author's later experiments d was taken as 0·031.

When $e = 3$ c.c. the reaction seems to be complete in 5 minutes, but, to be on the safe side, it is better to fix the minimum at 15 minutes.

The use of coal-gas is recommended by the author without passing it over alkaline pyrogallol or otherwise treating it before allowing it to pass through the apparatus.

The results obtained, however, can be made to vary, the extreme limit being less than 0·5 milligram of oxygen per litre of water, using 250 c.c. for the determination. To quote an extreme case. In one experiment (1), after the air has been wholly expelled from the bottle A, no more gas was passed through, and the titration was effected in the closed apparatus, the volumetric solution being run in as rapidly as possible. The end-reaction was not well defined. In the second experiment (2), the volumetric solution was run in very slowly drop by drop, and a brisk current of gas was kept passing through the apparatus. End-reaction well defined.

	Volume of Water.	Thiosulphate.	Oxygen per litre.
(1)	322 c.c.	15·35 c.c.	9·14 milligrams.
(2)	322 ,,	14·9 ,,	8·80 ,,

The difference is probably due to nearly all the oxygen dissolved in thiosulphate being used up in the first case, and being lost by diffusion in the second.

In the examination of waters from various sources, and making the experiments in pairs, using tubes of different sizes, the author found that exceedingly concordant results could easily be obtained.

In determining the oxygen in distilled water saturated with air, the author found that the results at 25° and 30° C. were higher than those obtained by Roscoe and Lunt, whilst at the lower temperatures they were almost identical, and it occurred to him that the difference was probably due to the mode of saturation. The agitation in a couple of Winchesters was done as directed by them, but the water used had been previously saturated at the lower temperatures, and probably were slightly super-saturated. A further series of experiments were then made with freshly-distilled water, which was not agitated with air until it had attained the desired temperature. The results proved that this surmise was correct. Probably some such explanation accounts for the uniformly higher results obtained by Dittmar.

No doubt there will be exceptional cases in which the process cannot be used, and others in which some modification may be required. A water containing nitrites will require the amount of the nitrous acid to be determined if the utmost accuracy is required. (A water containing one part of HNO_2 in 1,000,000, will affect the results + 0·17 milligram of oxygen per litre, 94 parts of the acid corresponding to 16 of oxygen.) Where nitrites are present in sufficient quantity to interfere, the amount may be determined by any of the ordinary processes, but the author prefers the following method :—

To 250 c.c. of the water to be examined, rendered faintly alkaline if not already so, add a few drops of strong solution of potassium iodide, and boil vigorously for a few minutes. Then transfer to the bottle A used in the oxygen determination, and allow to get quite cold in a slow current of coal gas. Then add a few drops of dilute sulphuric acid and solution of starch, and titrate with the thiosulphate. The correction to be made in the oxygen determination is thus ascertained. One or two experimental results may be quoted.

		Quantity of Water	Thiosulphate used.	Corrected.	Milligrams of Oxygen per litre.
1	Tap water . . .	232·5	13·2	9·7	10·43
2	Tap water + 5 milligrams commercial sodium nitrite . .	232·5	15·95	9·55	10·27
3	Tap water + 10 milligrams sodium nitrite	232·5	18·6	9·48	10·19

In number 2, the thiosulphate used by 250 c.c. of the boiled water was 2·8 c.c.

In number 3, the thiosulphate used by 250 c.c. of the boiled water was 5·45 c.c.

The results are fairly satisfactory, even with such large proportions of nitrite, proportions far larger than are likely to be met with in practice.

Nitrates do not interfere, even when present in large quantities; but fresh urine, when present to the extent of 1 per cent., has a small but very appreciable effect.

The following is an example of the method at ordinary temperature :—

Temperature 15° C.

	Quantity of Water taken.	Thiosulphate used	$c-b-cd.$	Milligrams of Oxygen per litre.	Difference from mean.
1	322·0	15·45	12·87	9·99	− 0·04
2	322·0	15·55	12·97	10·07	+ 0·04
3	232·5	11·90	9·43	10·14	+ 0·11
4	232·5	11·70	9·23	9·92	− 0·11
			Mean	10·03	

Barometer reading 760 mm.
10·03 milligrams = 7·02 c.c. at N.P.T.
Roscoe and Lunt found 6·96 c.c. at N.P.T. Difference + 0·06.

23. Winkler's Method as Modified by Rideal and Stewart[1] for Waters and Effluents.—The principle on which this method depends is the oxidation in an alkaline liquid of manganous oxide to a higher oxide of manganese, the subsequent liberation of iodine from potassium iodide by this in the acidified solution, and the titration of the liberated iodine by thiosulphate.

The following solutions are required:—

1. N/8 Permanganate (3·94 gm. $KMnO_4$ per litre).
2. Potassium oxalate (2 per cent. of the crystalline salt $K_2C_2O_4$, H_2O).
3. Manganous chloride (33 per cent. of the crystalline salt $MnCl_2$, $4H_2O$).
4. A mixed solution of caustic potash and potassium iodide containing 70 gm. KOH and 10 gm. KI per 100 c.c.
5. About N/20 sodium thiosulphate solution (about 12 gm. of the salt per litre).[2]

Concentrated sulphuric and hydrochloric acids are also required (the latter free from chlorine).

METHOD OF PROCEDURE: The temperature having been noted, a stoppered bottle of known capacity (300-350 c.c. when full) is completely filled with the sample of water or effluent (filtered or unfiltered, as may have been decided), avoiding any appreciable aeration in doing this, and 1 c.c. sulphuric acid is added, together with enough of the permanganate solution to leave a slight pink colour after the whole has been mixed and has stood for 10 minutes—the object being to oxidize any nitrite present to nitrate. If more than 10 c.c. of decinormal permanganate are required for this purpose, 2 c.c. of acid must be added instead of 1 c.c. The proper amount of permanganate to be added is best determined by a preliminary trial on 50 c.c. of the original liquid; this having been done, the amount required for the bottle-full is calculated and about 0·1 c.c. in excess of the calculated amount is added. The contents of the bottle are mixed by rotation and allowed to stand 10 minutes, after which any excess of permanganate is destroyed by the addition of 0·5 to 1·0 c.c. of the oxalate solution by means of a pipette, the neck filled up with the sample under examination, the stopper inserted, and the bottle rotated as before. The colour quickly disappears, and when decolorized 1 c.c. of the manganous chloride is passed to the bottom of the liquid from a long pipette, and immediately afterwards 3·0 c.c. of the mixed potash and iodide solution in the same manner. The stopper is inserted without air bubbles and the contents mixed by inversion and rotation. The liberated manganous hydroxide absorbs the free oxygen. On standing a few minutes the precipitated oxides of manganese settle; the stopper is then removed for a second and 5 c.c. of pure concentrated HCl (free from chlorine) are passed to the bottom by a pipette. The bottle is then closed and again rotated, and kept in the dark for 5 to 10 minutes, with frequent shaking, till clear. The liquid is then transferred to a porcelain dish and the iodine determined by thiosulphate and starch. The oxygen-equivalent of the latter being known, the amount of dissolved oxygen present in the sample is readily calculated. The reagents being used in the concentrated form with a comparatively large volume of water the correction for the additions is small and can usually be neglected. When, however, the oxygen is low, the reagents being presumably saturated with oxygen under atmospheric conditions, will make the result too high. The correction then to be applied is:

---

[1] *The Analyst*, 1901, **26**, 141.

[2] When standardizing, the weight of I equivalent to 1 c.c. of thiosulphate multiplied by 0·06303 (log. = $\bar{2}$·79956) gives the oxygen equivalent in grammes.

$$x = \frac{1000\,a - Rn}{V - n}.$$

Where x = no. of c.c. of oxygen at N.T.P. per litre of the liquid.
a = the amount of oxygen in c.c. found by titration.
V = the volume of the bottle.
n = the volume of the reagents.
R = no. of c.c. of oxygen contained in a litre of saturated water at the temperature of the experiment.

(R can be obtained from Roscoe and Lunt's table, or, preferably, is actually determined.)

NOTE.—1 gram of oxygen occupies 699·79 c.c. at N.T.P.

Winkler has described the following modification[1] as applicable to waters containing nitrites and organic substances which interfere with the process given above. To the bottle containing some of the water under examination, manganous chloride solution and sodium hydroxide solution free from potassium iodide are added in the usual way, and a current of carbon dioxide passed in. The manganous hydroxide is thus converted into manganous carbonate and manganous hydrogen carbonate; about 10 minutes' treatment with CO_2 is sufficient. The precipitate is now collected on a filter, washed with a 2 per cent. potassium bicarbonate solution, then dissolved in dilute hydrochloric acid containing potassium iodide, and the liberated iodine titrated with thiosulphate. The manganous carbonate is not oxidized by atmospheric oxygen during the filtration.

As a further improvement G. Bruhns[2] finds that if the liquid, after precipitation, completely clarifies on standing, the greater part may be siphoned off and only the residue treated with potassium iodide and acid. Long standing, however, is not desirable, as the result may be affected by impurities in the water. The author also states that the thiosulphate solution keeps well if made slightly alkaline to phenolphthalein.

The following details of procedure are taken from the Eighth Report of the Royal Commission on Sewage Disposal by Dr. G. McGowan, C. C. Frye and G. B. Kersaw[3]:—

For the determination of the dissolved oxygen taken up by effluents in 5 days it is recommended that, for purposes of a standard, the dilution should be 1 vol. of effluent plus 4 vols. of good tap water, and the test should be made in duplicate. A mixture of 4 vols. of water and 1 vol. of effluent will contain oxygen equivalent to about 4 to 4·5 parts per 100,000 of effluent, so that in the case of an effluent whose figure for dissolved oxygen absorption in 5 days does not exceed 2, something under 50 per cent. of the available oxygen will be required. This test involves the use of an incubator maintaining a temperature of 65° F. (18·3° C.). It is essential that the tap water with which the determinations are made should be at or close to 18° C. This is conveniently managed by filling a Winchester quart bottle about two-thirds full with water and keeping it at that temperature over night. The bottle must be well shaken up some little time before the determinations are made (not immediately before, as in that case the small air-bubbles would not have time to escape); this ensures the water not being supersaturated at that temperature. If the temperature of the effluent sample is below 18° C. it is to be brought to a temperature of about 18° C. just before the determination is made.

---

[1] *Z. a. C.*, 1914, **53**, 665.
[2] *Chem. Zeit.*, 1916, **40**, 985.
[3] Vol. II. Appendix, 1913 (Cd. 6943).

Method of Determination of Dissolved Oxygen Absorption in 5 Days.—Assuming the sample of effluent to have been taken in a half-Winchester quart bottle, the contents are thoroughly mixed and two portions of 200 c.c. each are poured into measuring flasks for the determination of suspended solids. The remainder of the effluent in the bottle is then well shaken for half a minute or so, in order to bring its dissolved oxygen content to something near that of the diluting water. The effluent is then diluted with 4 times its volume of tap water (note precautions given above) in a capacious flask. The contents of the flask are then gently but thoroughly mixed and four clean (marked) bottles, of 340 to 360 c.c. capacity when quite full,[1] are filled quietly and quickly with the diluted effluent, a little being allowed to overflow. The bottles are left unstoppered for 5 minutes, any tiny air bubbles in the shoulder of the bottle removed by tilting, then stoppered, being completely full of liquid. Two of the bottles are placed in the incubator for 5 days, while in the other two the oxygen in solution is at once determined as follows:—

0·9 c.c. of sulphuric acid is added, and then sufficient of the permanganate solution to leave a slight excess of the latter after the whole has been mixed and has stood for 20 minutes (stoppered, of course); 1 to 2 c.c. of the permanganate are nearly always sufficient for this. After 20 minutes standing (not less), the excess of permanganate is destroyed by the addition of about 1 c.c. of oxalate solution, the bottle being at once restoppered and its contents mixed.

When the liquid has become colourless, the stopper is again removed and 1 c.c. of manganous chloride is run in from a pipette at the bottom of the bottle, followed immediately by 4 c.c. of the caustic potash and potassium iodide solution; in this latter case the point of the pipette need be only a little below the surface of the liquid. The stopper having been again inserted, the bottle is turned over once or twice to mix the contents, and after a few minutes turned over again and allowed to stand for a further few minutes; this ensures good settlement of the hydroxides of manganese. 5 c.c. of HCl are now run in from a pipette, and the bottle is re-stoppered and kept in the shade for 5 to 10 minutes, with occasional rotation. 20 c.c. of the liquid are now pipetted out of the bottle and rejected, and the remainder is titrated with thiosulphate, using some *clear* starch solution towards the end of the titration.

---

[1] In cold weather these bottles must be warmed to about 18° C. before use.

At the end of 5 days the oxygen remaining in solution in the incubated samples is determined in the same way.

The difference between the two determinations represents the oxygen taken up by the effluent in the interval.

Ex. One vol. of effluent is mixed with 4 vols. of tap water and incubated.

Dissolved oxygen in the mixture at start :—

Vol. of bottle 341 − 20 = 321 c.c.

Thiosulphate used = 6·95 c.c. (1 c.c. = ·0003773 grm. oxygen).

Hence dissolved oxygen

$$= \frac{0\cdot0003773 \times 6\cdot95 \times 100000}{321} = 0\cdot817 \text{ part per } 100{,}000.$$

Dissolved oxygen after incubation :—

Vol. of bottle 338 − 20 = 318 c.c.

Thiosulphate used = 4·1 c.c.

This gives 0·488 part dissolved oxygen per 100,000. Hence, dissolved oxygen taken up by the mixture is

$$0\cdot817 - 0\cdot488 = 0\cdot329 \text{ part per } 100{,}000.$$

As the mixture was only $\frac{1}{5}$ effluent, the dissolved oxygen taken up by the effluent is $0\cdot329 \times 5 = 1\cdot65$ parts by weight per 100,000.

24. Method of Recording Water and Sewage Examination Results.

The report[1] of the committee appointed to establish a Uniform System of recording the Results of the Chemical and Bacterial Examination of Water and Sewage is as follows: That it is desirable that results of analysis should be expressed in parts per 100,000 except in the case of dissolved gases, when these should be stated as cubic centimetres of gas at 0° C., and 760 millimetres in 1 litre of water. This method of recording results is in accordance with that suggested by the committee appointed in 1887 to confer with the committee of the American Association for the Advancement of Science, with a view to forming a uniform system of recording the results of water analysis.

The committee suggest that in the case of all nitrogen compounds the results be expressed as parts of nitrogen over 100,000, including the ammonia expelled on boiling with alkaline permanganate, which should be termed albuminoid nitrogen. The nitrogen will therefore be returned as :

(1) Ammoniacal nitrogen from free and saline ammonia.

(2) Nitrous nitrogen from nitrites.

(3) Nitric nitrogen from nitrates.

(4) Organic nitrogen (either by Kjeldahl or by combustion, but the process used should be stated).

(5) Albuminoid nitrogen.

The total nitrogen of all kinds will be the sum of the first four determinations.

---

[1] British Association Report, 1899.

The committee are of opinion that the percentage of nitrogen oxidized—that is, the ratio of (2) and (3) to (1) and (4)—gives sometimes a useful measure of the stage of purification of a particular sample. The purification effected by a process will be measured by the amount of oxidized nitrogen as compared with the total amount of nitrogen existing in the crude sewage.

In raw sewage and in effluents containing suspended matter, it is also desirable to determine how much of the organic nitrogen is present in the suspended matter.

In sampling, the committee suggest that the bottles should be filled nearly completely with the liquid, only a small air-bubble being allowed to remain in the neck of the bottle. The time at which a sample is drawn, as well as the time at which its analysis is begun, should be noted. An effluent should be drawn to correspond as nearly as possible with the original sewage, and both it and the sewage should be taken in quantities proportional to the rate of flow when that varies (*e.g.*, in the emptying of a filter-bed).

In order to avoid the multiplication of analyses, the attendant at a sewage works (or any other person who draws the samples) might be provided with sets of twelve or twenty-four stoppered quarter-Winchester bottles, one of which should be filled every hour or every 2 hours, and on the label of each bottle the rate of flow at the time should be written. When the bottles reach the laboratory, quantities would be taken from each proportional to these rates of flow and mixed together, by which means a fair average sample for the 24 hours would be obtained.

The committee at present are unable to suggest a method of reporting bacterial results, including incubator tests, which is likely to be acceptable to all workers.

Rules for Converting Parts per 100,000 into Grains per Gallon and Vice Versa.

To convert—

Parts per 100,000 into grains per gallon, multiply by 0·7.
Grains per gallon into parts per 100,000, divide by 0·7.
Grams per litre into grains per gallon, multiply by 70.

25. Standards for Sewage Effluents.

In 1898 a Royal Commission was appointed to inquire and report what methods of treating and disposing of sewage (including any liquid from any factory or manufacturing process) may properly be adopted. An Interim Report was issued in 1901, followed by eight subsequent Reports, which appeared from time to time from 1902 to 1913. Provisional standards for judging the purity of effluents were given in the Fifth Report, and are to be found in the Tenth Edition of this book. These, however, have been superseded by the conclusions stated in the Eighth Report (1912), which were confirmed in the Final Report (1915).[1]

---

[1] [Cd. 7821.]

The most important results arrived at may briefly be summarized as follows:

The nuisance-producing power of a normal sewage or effluent is proportional to its power of deoxygenating the water of the stream into which it is discharged.

The dissolved oxygen absorption test provides the most trustworthy chemical index of the actual state of a stream and should be adopted for purposes of a standard.

The standard adopted for a river water is an absorption of not more than 0·4 part of dissolved oxygen per 100,000 in 5 days at the temperature of 65° Fahr.

This figure (0·4) is termed the "limiting figure" and forms the foundation upon which the scheme of standards is constructed.

A mixture complying with the above standard may be expressed in the form of an equation as follows:

$$\frac{x + yz}{z + 1} = 0{\cdot}4,$$

where x = parts of dissolved oxygen per 100,000 taken up by effluent
y = „ „ „ „ „ river water above outfall.
z = dilution (proportion of river water to effluent).

Thus, if an effluent is discharged into 10 times its volume of a very clean river water which itself takes up only 0·1 part of dissolved oxygen in 5 days, the equation becomes

$$\frac{x + (0{\cdot}1 \times 10)}{10 + 1} = 0{\cdot}4$$

$$x + 1 = 4{\cdot}4$$

$$x = 3{\cdot}4$$

i.e., the effluent may be permitted to take up 3·4 parts of dissolved oxygen per 100,000 in 5 days, and that figure would be the standard for that particular discharge.

A river of average purity shows an absorption of 0·2 part per 100,000 of dissolved oxygen in 5 days. Hence for purposes of calculation as above this value should be assumed to be constant and represented by the figure 0·2.

For administrative reasons a fixed general standard should be relaxed or made more stringent as local circumstances permitted or required.

This general or normal standard for effluents is thus defined:

An effluent, in order to comply with the general standard, must not contain as discharged more than 3 parts per 100,000 of suspended matter, and with its suspended matters included must not take up at 65° F. (18·3° C.) more than 2·0 parts per 100,000 of dissolved oxygen in 5 days.

The following analyses[1] of effluents may be found useful:—

---

[1] From Rideal and Burgess's paper on "The New Standards for Sewage Effluents," *Analyst*, **34**, 1909, 201.

(Parts per 100,000.)	Effluent from Land.	Effluent from Land	Effluent from Bacterial Treatment.	Effluent from Bacterial Treatment.
Total solids	64·1	86·4	70·3	53·4
Suspended matter, total	Less than 3	Less than 3	Less than 3	4·40
,, ,, volatile	—	—	—	2·98
,, ,, non-volatile	—	—	—	1·42
Ammonia, free	0·58	0·53	0·95	0·22
,, albuminoid	0·26	0·075	0·13	0·17
Oxygen absorbed from permanganate:				
In 3 minutes at 80° F.	—	—	—	0·80
In 4 hours at 80° F.	0·65	0·65	1·38	2·23
Nitrogen as nitrates	1·09	1·61	2·73	1·95
,, nitrites	0·015	0·04	0·02	0·03
Chlorine	6·1	7·1	6·7	5·5
Dissolved oxygen absorbed:				
(*a*) in 24 hours	0·3	0·0	0·0	0·02
(*b*) in 48 hours	0·8	0·04	0·30	0·06
(*c*) in 5 days	1·4	0·28	0·72	0·22

26. THE PREPARATION OF REAGENTS.

A. Reagents required for the Determination of Nitrogen present as Ammonia, Free and Saline, and Albuminoid.

(i) **Nessler's Solution.**—Dissolve 62·5 gm. of potassium iodide in about 250 c.c. of distilled water, set aside a few c.c. and add gradually to the larger part a cold saturated solution of mercuric chloride (of which about 500 c.c. will be required) until the mercuric iodide precipitated ceases to be redissolved on stirring. When a permanent precipitate is obtained, restore the reserved potassium iodide so as to redissolve it, and continue adding mercuric chloride very gradually until a slight precipitate remains undissolved. (The small quantity of potassium iodide is set aside merely to enable the mixture to be made rapidly without danger of adding an excess of mercury.)

Next dissolve 150 gm. of solid potassium hydrate (that usually sold in sticks or cakes) in 150 c.c. of distilled water, allow the solution to cool, add it gradually to the above solution, and make up with distilled water to one litre.

On standing, a brown precipitate is deposited, and the solution becomes clear, and of a pale greenish-yellow colour. It is ready for use as soon as it is perfectly clear, and should be decanted into a smaller bottle as required. The reagent improves on keeping.

The British Pharmacopœia, 1914, gives the following directions for making this reagent:—

Potassium iodide	35 gm.
Mercuric chloride	q.s.
Sodium hydroxide	120 gm.
Distilled water to	1 litre

Dissolve the iodide and 12·5 gm. of mercuric chloride in 800 c.c. of water, and to this liquid add a cold saturated aqueous solution of mercuric chloride, with constant stirring, until a slight red precipitate remains. Add the sodium hydroxide and dissolve, then add a little more of the solution of mercuric chloride, and sufficient water to produce the required volume.

This formula is more economical than the above, and is satisfactory.

(ii) **Standard Solution of Ammonium Chloride.**—Dissolve 1·9093 gm. of pure dry ammonium chloride in a litre of distilled water; of this take 100 c.c., and make up to a litre with distilled water. The latter solution will contain ammonia corresponding to 0·00005 gm. of nitrogen in each c.c. In use it should be measured from a narrow burette of 10 c.c. capacity divided into tenths, or from a 1 c.c. pipette. Ammonia-free distilled water must be used for making the solution.

[If it is desired to determine "*ammonia*" rather than "*nitrogen as ammonia*" take 1·5708 gm. of ammonium chloride instead of 1·9093 gm.; 1 c.c. will then correspond to 0·00005 gm. of ammonia (NH_3).]

(iii) **Sodium Carbonate.**—Heat anhydrous sodium carbonate in a platinum crucible for about an hour, taking care not to fuse it. While still warm rub it in a clean mortar so as to break any lumps which may have been formed, and transfer to a clean dry wide-mouthed stoppered bottle.

(iv) **Water free from Ammonia.**—If, when 2 c.c. of Nessler's solution (A. i) is added to 100 c.c. of distilled water in a glass cylinder, standing on a white surface (see Determination of Ammonia), no trace of a yellow tint is visible after 5 minutes, the water is sufficiently pure for use. As, however, this is rarely the case, the following process must usually be adopted. Distil from a large glass retort (or better, from a copper or tin vessel holding 15 to 20 litres) ordinary distilled water which has been rendered distinctly alkaline by addition of sodium carbonate. A glass Liebig condenser or a clean tin worm should be used to condense the vapour; it should be connected to the still by a short india-rubber joint. Test the distillate from time to time with Nessler's solution, as above described, and when free from ammonia collect the remainder for use. The distillation must not be carried to dryness. Ordinary water may be used instead of distilled water, but it occasionally continues for some time to give off traces of ammonia by the slow decomposition of the organic matter present in it.

J. Barnes[1] has pointed out that distilled water can be completely freed from ammonia by adding a little bromine and boiling for a few minutes. More rapid is the action of alkaline hypobromite in the cold. Enough bromine is added to the water to give it a perceptible tint, and then a drop of sodium hydroxide solution; after 10 minutes a little potassium iodide is added to remove the undecomposed hypobromite, and the water is then fit for use in the determination of ammonia by Nessler's test.

(v) **Alkaline Permanganate Solution.**—Dissolve 200 gm. of stick potash[1] in water in a large porcelain dish and add a solution of 8 gm. of potassium permanganate in water, using 1100 c.c. altogether. Boil rapidly until concentrated to about 900 c.c., add about 200 c.c. of hot distilled water, and continue boiling till the volume is reduced to a litre. When cool pour at once into a bottle. Every fresh lot of solution made should be carefully tested before being used.

---

[1] *J. S. C. I.*, 1896, **15**, 254-255.

B. Reagents required for the Determination of Nitrogen present as Nitrates and Nitrites (Crum's Process).

(i) **Concentrated Sulphuric Acid.**—This must be free from nitrates and nitrites.

(ii) **Potassium Permanganate.**—Dissolve about 10 gm. of crystallized potassium permanganate in a litre of distilled water.

(iii) **Sodium Carbonate.**—Dissolve about 10 gm. of dry, or an equivalent quantity of crystallized, sodium carbonate, free from nitrates, in a litre of distilled water.

For the Determination of Nitrogen as Nitrates and Nitrites in Waters containing a very large quantity of Soluble Matter, but little Organic Nitrogen.

(iv) **Metallic Aluminium.**—As thin foil.

(v) **Solution of Sodium Hydrate.**—Dissolve 100 gm. of stick soda in a litre of distilled water; when cold, put it in a tall glass cylinder, and introduce about 100 sq. cm. of aluminium foil, which must be kept at the bottom of the solution by means of a glass rod. When the aluminium is dissolved, boil the solution briskly in a porcelain basin until about ⅓ of its volume has been evaporated, allow to cool, and make up to its original volume with water free from ammonia. The absence of nitrates is thus ensured.

(vi) **Broken Pumice.**—Clean pumice is broken in pieces of the size of small peas, sifted free from dust, heated to redness for about an hour, and kept in a closely stoppered bottle.

(vii) **Hydrochloric Acid free from Ammonia.**—The acid sold as "pure for analysis" is nearly always quite free from ammoniacal contamination. Only 2 or 3 drops are required for each experiment

For the Determination of Nitrites by Griess's Process.

(viii) **Metaphenylene-diamine.**—A half per cent. solution of the base in very dilute sulphuric or hydrochloric acid. The base alone is not permanent. If too highly coloured, it may be bleached by pure animal charcoal.

(ix) **Dilute Sulphuric Acid.**—One volume of acid to two of water.

(x) **Standard Potassium or Sodium Nitrite.**—Dissolve 0·405 gm. of pure silver nitrite in boiling distilled water, and add pure potassium or sodium chloride till no further precipitate of silver chloride is formed. Make up to a litre; let the silver chloride settle, and dilute 100 c.c. of the clear liquid to a litre. It should be kept in small stoppered bottles completely filled, and in the dark.

---

[1] The equivalent amount of caustic soda, viz. 143 gm., may be substituted.

1 c.c. = 0·01 mgm. N_2O_3.
(By using 1·100 gm. of silver nitrite instead of 0·405 gm.
1 c.c. = 0·01 mgm. nitrogen.)

The colour produced by the reaction of nitrous acid on metaphenylene-diamine is triamidoazo-benzene, or " Bismarck brown ".

C. Reagents required for the Determination of combined Chlorine.

(i) **Standard Solution of Silver Nitrate.**—Dissolve 2·4 gm. of re-crystallized silver nitrate in a litre of distilled water and standardize against a solution of pure sodium chloride containing 0·8243 gm. per litre (1 c.c. = 0·0005 gm. chlorine). 1 c.c. silver nitrate solution = 0·0005 gm. Cl, or when 50 c.c. of water are titrated, 1 c.c. = 1 part of combined chlorine per 100,000.

(ii) **Solution of Potassium Chromate.**—A strong solution of pure neutral potassium chromate free from chlorine. It is most conveniently kept in a bottle with a ground glass cap and provided with a small dropping-tube.

D. Reagents required for Determination of Hardness by Clark's Method.

(i) **Standard Solution of Calcium Chloride.**—Dissolve in dilute hydrochloric acid, in a platinum dish, 0·2 gm. of pure crystallized calcite, adding the acid gradually, and having the dish covered with a glass plate, to prevent loss by spurting. When all is dissolved, evaporate to dryness on a water-bath, add a little distilled water, and again evaporate to dryness. Repeat the evaporation several times to ensure complete expulsion of free acid. Lastly, dissolve the calcium chloride in distilled water, and make up to one litre.

50 c.c. correspond to 0·01 gm. $CaCO_3$.

(ii) **Standard Solution of Potassium Soap.**—Weigh out 50 gm. of commercial oleic acid in a beaker and add 100 c.c. of an alcoholic potash solution made by dissolving 20 gm. of stick potash in 180 c.c. of *industrial* methylated spirit[1] and continue adding the same solution from a burette till a drop of the oleate just gives a red colour with phenolphthalein spotted on a white plate—about 10 c.c. more being required. Measure the solution and make the volume to 400 c.c. by the addition of industrial methylated spirit. 45 c.c. of the strong soap solution thus obtained are diluted with methylated spirit (2 vols.) and water (1 vol.) to a litre, allowed to stand for about 24 hours, filtered through a double Swedish filter and standardized against standard calcium chloride solution. The solution will be found a little too strong, and is diluted as before to exact strength, which is attained when 14·25 c.c. are required to form a permanent lather with 50 c.c. of the standard calcium chloride solution. The process is carried out exactly as in determining the hardness of a water. (When diluting the soap solution to exact strength, add the requisite amount of methylated spirit and water mixed—not separately.)

---

[1] " Industrial methylated spirit " is a duty-free alcohol that has been denatured by the addition of crude methyl alcohol or wood spirit, of which it contains 5 per cent.—and no petroleum-spirit.

E. Reagents required for the Determinaton of Oxygen absorbed.

Standard Solution of Potassium Permanganate.—Dissolve 0·395 gm. of pure potassium permanganate in 1000 c.c. of water. Each c.c. contains 0·0001 gm. of available oxygen.

Potassium Iodide Solution.—One part of the pure salt dissolved in 10 parts of distilled water.

Dilute Sulphuric Acid.—One part by volume of pure sulphuric acid is mixed with 3 parts by volume of distilled water, and solution of potassium permanganate dropped in until the whole retains a *very faint* pink tint, after warming to 80° F. for 4 hours.

Sodium Thiosulphate.—One gm. of the pure crystallized salt dissolved in 1000 c.c. of water.

Starch Indicator.—The best form in which to use this is the solution described on p. 137.

27. Characteristics of Waters derived from various Geological Formations.

Dr. Rideal[1] gives the following useful summary of the above:—

Hard Waters, as a rule, are furnished by the following formations: Calcareous strata of Silurian, Devonian or Old Red Sandstone, and Coal Measures, Mountain Limestone, Lias, Oolite, Upper Greensand, Chalk. **Soft Waters,** by Igneous, Metamorphic, non-calcareous Cambrian, Silurian, Devonian, and Coal Measures, Lower Greensand, London and Oxford Clay, Bagshot Beds (hardness 1-9, average 4), and non-calcareous gravel. Water from Gault Clay varies very much: some of it is soft and pure, some of "fair quality," hardness 9-11 degrees; in Bedfordshire it often contains much lime and iron, derived from pyrites and coprolites. Lower Greensand and shale waters are frequently very ochreous. Water from Oxford and Kimmeridge Clays contains much vegetable matter, and is sometimes bituminous; other clays often include much sulphate of lime and give waters of high permanent hardness. The new Red Sandstone waters are generally briny and quite unfit for drinking, besides containing much sulphate of lime and magnesium salts. Magnesian limestone (Dolomite) also yields usually a bad supply. The water in porous strata below the central portions of clay basins is usually bad, containing much alkali chloride and sulphate, and also sodium carbonate, due to the rain having percolated laterally through a large body of soil before reaching the spot, and having dissolved and accumulated the soluble constituents: from the presence of alkali carbonate the lime is generally low, and there is often little organic matter.

---

[1] *Water and its Purification*, pp. 259-260. Detailed information on this topic is given in an appendix to the book.

28. THE INTERPRETATION OF THE RESULTS OF ANALYSIS.

All figures refer to **parts per 100,000.**

The primary form of natural water is rain, the chief impurities in which are traces of organic matter, ammonia, and ammonium nitrate derived from the atmosphere. On reaching the ground it becomes more or less charged with the soluble constituents of the soil, such as calcium and magnesium carbonates, potassium and sodium chlorides, and other salts, which are dissolved, some by a simple solvent action, others by the agency of carbonic acid in solution. Draining off from the land, it will speedily find its way to a stream which, in the earlier part of its course, will probably be free from pollution by animal matter, except that derived from any manure which may have been applied to the land on which the rain fell. Thus comparatively pure, it will furnish to the inhabitants on its banks a supply of water which, after use, will be returned to the stream in the form of sewage charged with impurity derived from animal excreta, soap, household refuse, etc., the pollution being perhaps lessened by submitting the sewage to some purifying process, such as irrigation of land, filtration, or clarification. The stream in its subsequent course to the sea will be in some measure purified by slow oxidation of the organic matter, and by the absorbent action of vegetation. Some of the rain will not, however, go directly to a stream, but sink through the soil to a well. If this be shallow it may be considered as merely a pit for the accumulation of drainage from the immediately surrounding soil, which, as the well is in most cases close to a dwelling, will be almost inevitably charged with excretal and other refuse; so that the water when it reaches the well will be contaminated with soluble impurities thence derived, and with nitrites and nitrates resulting from their oxidation. After use the water from the well will, like the river water, form sewage, and find its way to a river, or again to the soil, according to circumstances.

In the case of a deep well, from which the surface water is excluded, the conditions are different. The shaft will usually pass through an impervious stratum, so that the water entering it will not be derived from the rain which falls on the area immediately surrounding its mouth, but from that which falls on the outcrop of the pervious stratum below the impervious one just mentioned; and if this outcrop be in a district which is uninhabited and uncultivated, the water of the well will probably be entirely free from organic impurity or products of decomposition. But even if the water be polluted at its source, still it must pass through a very extensive filter before it reaches the well, and its organic matter will probably be in great measure converted by oxidation into bodies in themselves innocuous.

This is very briefly the general history of natural waters, and the problem presented to the analyst is to ascertain, as far as possible, from the nature and quantity of the impurities present, the previous history of the water, and its present condition and fitness for the purpose for which it is to be used.

It is impossible to give any fixed rule by which the results obtained by the foregoing method of analysis should be interpreted. The analyst must form an independent opinion for each sample from a consideration of all the results he has obtained. Nevertheless, the following remarks will probably be of service.

Total Solid Matter.

Waters which leave a large residue on evaporation are, as a rule, less suited for general domestic purposes than those which contain less matter in solution, and are unfit for many manufacturing purposes. The amount of residue is also of primary importance as regards the use of the water for steam boilers, as the quantity of incrustation produced will chiefly depend upon it. It may vary considerably, apart from any unnatural pollution of the water, as it depends principally on the nature of the soil through or over which the water passes. River water, when but slightly polluted, contains generally from 10 to 40 parts. Shallow well water varies greatly, containing from 30 to 150 parts, or even more, the proportion here depending less on the nature of the soil than on the original pollution of the water. Deep well water also varies considerably; it usually contains from 20 to 70 parts, but this range is frequently overstepped, the quantity depending largely upon the nature of the strata from which the water is obtained. Spring waters closely resemble those from deep wells. Sewage contains generally from 50 to 100 parts, but occasionally less, and frequently much more. The total solid matter, as a rule, exceeds the sum of the constituents determined; the nitrogen, as nitrates and nitrites, being calculated as potassium nitrate, and the chlorine as sodium chloride; but occasionally this is not the case, owing, it is likely, to the presence of some of the calcium as nitrate or chloride.

Nitrogen as Ammonia.

The ammonia in natural waters is derived almost exclusively from animal contamination, and its quantity varies between very wide limits. In upland surface waters it seldom exceeds 0·008 part, the average being about 0·002 part. In water from cultivated land the average is about 0·005, and the range is greater, being from *nil* to 0·025 part, or even more. In water from shallow wells the variation is so great that it would be useless to attempt to state an average, all proportions from *nil* to as much as 2·5 parts having been observed. In waters from deep wells a very considerable proportion is often found, amounting to 0·1 part or even more, the average being 0·01 part, and the variations considerable. In spring water it is seldom that more than 0·01 part of nitrogen as ammonia occurs, the average being only 0·001 part. Sewage usually contains from 2 to 6 parts, but occasionally as much as 9 or 10 parts, the average being about five. Ammonia is readily oxidized to nitrites and nitrates, and hence its presence, in considerable quantity, usually indicates the absence of oxidation, and is generally coincident with the presence of organic matter. That sometimes found in waters from very deep wells is, however, probably due to subsequent decomposition of nitrates.

Albuminoid Ammonia.

Wanklyn's standards for albuminoid ammonia are

High purity,	0·0 to 0·0041	parts per 100,000.
Satisfactory,	0·0041 to 0·0082	,, ,,
Impure,	over 0·0082	,, ,,

In the absence of free ammonia, he does not condemn a water unless the albuminoid exceeds ·0082, but a water yielding ·0123 he condemns in any circumstances. When the albuminoid ammonia process was introduced it was well known that there was a varying relation between the quantities of albuminoid ammonia and the amounts of different kinds of nitrogenous organic matter. The researches of numerous chemists have confirmed the inference that, although a useful indication, too much importance must not be attached to this figure.

Nitrogen as Nitrates and Nitrites.

Nitrates and nitrites are produced by the oxidation of nitrogenous organic matter, and almost always from animal matter. In upland surface waters the proportion varies from *nil* to 0·05 part or very rarely more, but the majority of samples contain none or mere traces, the average being about 0·009 part. In surface waters from cultivated land the quantity is much greater, varying from *nil*, which seldom occurs, to 1 part, the average being about 0·25 part. The proportion in shallow wells is usually much greater still, ranging from *nil*, which very rarely occurs, to as much as 25 parts. It would probably be useless to attempt to state an average, but quantities of from 2 to 5 parts occur most frequently. In water from deep wells the range is from *nil* to about 3 parts, and occasionally more, the average being about 0·5 part. In spring water the range is about the same as in deep well water, but the average is somewhat lower.

It sometimes happens that, when the supply of atmospheric oxygen is deficient, the organic matter in water is oxidized at the expense of the nitrates present; and occasionally, if the quantities happen to be suitably proportioned, they are mutually destroyed, leaving no evidence of pollution. This reduction of nitrates often occurs in deep well water, as for example, in that from wells in the Chalk beneath London Clay, where the nitrates are often totally destroyed. In sewages, putrefaction speedily sets in, and during this condition the nitrates are rapidly destroyed, and so completely and uniformly that it is probably needless to attempt their determination, except in sewages which are very weak, or for other special reasons abnormal. Out of a large number of samples, only a very few have been found which contained any nitrates, and those only very small quantities.

Nitrites occurring in deep springs or wells no doubt arise from the deoxidation of nitrates by ferrous oxide, or certain forms of organic matter of a harmless nature; but whenever they occur in shallow wells or river water, they may be of much greater significance. Their presence in such cases is most probably due to recent sewage contamination, and such waters must be looked upon with great suspicion.

"In the ordinary course of nitrification in nature the ammonia is wholly converted into nitrite, the preliminary oxidation to nitrite being rapidly passed over, but if water containing nitrates is brought into contact with organic matter, these nitrates become more or less reduced to nitrites through the agency of certain micro-organisms, and hence the presence of nitrites generally constitutes evidence of contamination with organic matter subsequent to the original nitrification, rather than to the latter having been imperfect. The fact must also not be lost sight of that nitrates can be reduced by certain microbes in the presence of organic matter with elimination of the nitric nitrogen in the free state, or as oxides of nitrogen, and that a contamination of the nitrified water may thus lead to the more or less complete removal of the mineral nitrogen. The absence of nitrates may thus, in some circumstances, actually indicate contact with animal matter instead of freedom from it" (P. F. Frankland; Warington; Munro).

Total Inorganic Nitrogen.

When organic matter is oxidized it is ultimately resolved into inorganic substances. Its carbon appears as carbonic acid, its hydrogen as water, and its nitrogen as ammonia, nitrous acid, or nitric acid; the last two combining with the bases always present in water to form nitrites and nitrates. The carbon and hydrogen are thus clearly beyond the reach of the analyst; but the nitrogen compounds, as has been shown, can be accurately determined, and furnish us with a means of estimating the amount of organic matter which was formerly present in the water, but which has already undergone decomposition.

The sum of the amounts of nitrogen found in these three forms constitutes then a distinct and valuable term in the analysis, the *organic* nitrogen relating to the *present*, and the total *inorganic* nitrogen to the *past* conditions of the water. Since ammonia, nitrites, and nitrates are quite innocuous, the total inorganic nitrogen does not indicate *actual* evil like the organic nitrogen, but *potential* evil, as it is evident that the innocuous character of a water which contains much nitrogen in these forms depends wholly on the permanence of the conditions of temperature, aeration, filtration through soil, etc., which have broken up the original organic matter; if these should at any time fail, the *past* contamination would become *present*, the nitrogen appearing in the organic form, the water being loaded in all likelihood with putrescent and contagious matter.

In upland surface waters which have not been contaminated to any extent by animal pollution the total inorganic nitrogen rarely exceeds 0·03 part. In water from cultivated districts the amount is greater, ranging as high as 1 part, the average of a large number of samples being about 0·22 part. It is useless to attempt any generalization for shallow wells, as the proportion depends upon local circumstances. The amount is usually large and may reach the enormous quantity of 25 parts per 100,000. Waters containing 1 to 5 parts are very commonly met with. In water from deep wells and springs, quantities ranging up to 3·5 parts have been observed, the average on a large series of analyses being 0·5 part for deep wells, and about 0·4 part for springs.

It must be remembered that the conditions attending deep wells and springs are remarkably permanent, and the amount of filtration which the water undergoes before reaching the well itself, or issuing from the spring is enormous. Meteorological changes here have either no effect, or one so small and slow as not to interfere with any purifying actions which may be taking place. All other sources of water, and especially shallow wells, are on the other hand subject to considerable changes A sudden storm after drought will wash large quantities of polluting matter into the water-course; or dissolve the filth which has been concentrating in the pores of the soil during the dry season, and carry it into the well. Small indications therefore of a polluted origin are very serious in surface waters and shallow well waters, but are of less moment in water from deep wells and springs; the *present* character of these being of chief importance, since whatever degree of purification may be observed, may usually be treated as permanent.

Chlorine.

This is usually present as sodium chloride, but occasionally, as has been mentioned before, it occurs as a calcium salt. It is derived, in some cases, from the soil, but more usually from animal excreta (human urine contains about 500 parts per 100,000), and is therefore of considerable importance in forming a judgment as to the character of a water. Unpolluted river and spring waters usually contain less than 1 part; average town sewage about 11 parts. Shallow well water may contain any quantity from a mere trace up to 50 parts or even more. Its amount is scarcely affected by any degree of filtration through soil; thus the effluent water from land irrigated with sewage contains the same proportion of chlorine as the sewage, unless it has been diluted by subsoil water or concentrated by evaporation. Of course, attention should be given to the geological nature of the district from which the water comes, the distance from the sea or other source of chlorine, etc., in order to decide on the origin of the chlorine.

Hardness.

This is chiefly of importance as regards the use of the water for cleansing and manufacturing operations, and for steam boilers. It is still a moot point as to the effect on health of hard and soft drinking waters respectively. The "temporary" hardness is due to carbonates of lime and magnesia held in solution by carbonic acid. On boiling, the CO_2 is driven off and the carbonates deposited. Water free from CO_2, however, dissolves carbonate of lime and carbonate of magnesia, each in the proportion of about 3 parts per 100,000. To this extent, therefore, these salts may form part of the "permanent" hardness, which is mainly due to the presence of sulphates, chlorides and nitrates of lime and magnesia. "Permanent" hardness is not removed by boiling. As the hardness depends chiefly on the nature of the soil through and over which the water passes, the variations in it are very great; that from igneous strata has least hardness, followed in approximate order by that from Metamorphic, Cambrian, Silurian and Devonian rocks, Millstone

Grit, London Clay, Bagshot Beds, New Red Sandstone, Coal Measures, Mountain Limestone, Oolite, Chalk, Lias, and Dolomite, the average in the case of the first being 2·4 parts, and of the last 41 parts. As animal excreta contain a considerable quantity of lime, highly polluted waters are usually extremely hard. Water from shallow wells contains varying proportions up to nearly 200 parts of total hardness. No generalization can be made as to the proportion of permanent to temporary hardness.

Suspended Matter.

This is of a less degree of importance than the matters hitherto considered. From a sanitary point of view it is of minor interest, because it may be in most cases readily and completely removed by filtration. Mineral suspended matter is, however, of considerable mechanical importance as regards the formation of impediments in the river bed by its gradual deposition, and as regards the choking of the sand filters in water-works; and organic suspended matter is at times positively injurious, and always favours the growth of minute organisms.

General Considerations.

From the determinations which have been described, it is believed that a sound judgment as to the character of a water may be made, and the analyst should hardly be content with a less complete examination. If, however, from lack of time or other cause, so much cannot be done, a tolerably safe opinion may be formed, omitting the determination of total solid matter and hardness.

In judging of the character of a sample of water, due attention must of course be paid to the purpose for which it is proposed to be used. The analyst frequently has only to decide broadly whether the water is good or bad; as, for example, in cases of the domestic supply to isolated houses or of existing town supplies. Water which would be fairly well suited for the former might be very objectionable for the latter, where it would be required to a certain extent for manufacturing purposes. Water which would be dangerous for drinking or cooking may be used for certain kinds of cleansing operations; but it must not be forgotten that unless great care and watchfulness are exercised there is considerable danger of this restriction being neglected, and especially if the objectionable water is nearer at hand than the purer supply.

It is often required to decide between several proposed sources of supply, and here great care is necessary, especially if the differences between the samples are not great. If possible, samples should be examined at various seasons of the year; and care should be taken that the samples of the several waters are collected as nearly as possible simultaneously and in a normal condition. The general character of a water is most satisfactorily shown by the average of a systematic series of analyses. River waters should, as a rule, not be examined immediately after a heavy rain when they are in flood. A sudden rainfall after a dry season will often foul a river more than a much heavier and more prolonged downfall after average weather. Similarly the sewage discharged from a town at the beginning of a heavy rainstorm is usually extremely foul, the solid matter which has been accumulating on the sides of the sewers, and in corners and recesses, being rapidly washed out by the increased stream.

The possibility of *improvement* in quality must also be considered. A turbid water may generally be rendered clear by filtration, and this will often also effect some slight reduction in the quantity of organic matter; but while somewhat rapid filtration through sand or similar material will usually remove all solid suspended matter, it is generally necessary to pass the water very slowly through a more efficient filtering material to destroy any large proportion of the organic matter in solution. Very fine sand, animal charcoal, and spongy iron are all in use for this purpose. The quantity of dissolved oxygen must not be neglected in considering the question of filtration. If the water contains only a small quantity of organic matter and is well aërated, the quantity of oxygen in solution may be sufficient, and the filtration may then be continuous; but in many instances this is not the case, and it is then necessary that the filtration should be intermittent, the water being allowed at intervals to drain off from the filtering material in order that the latter may be well aërated, after which it is again fit for work.

Softening water by Clark's process generally removes a large quantity of organic matter from solution, it being carried down with the calcium carbonate precipitate.

It is evident that no very definite distinction can be drawn between deep and shallow wells. In the foregoing pages, deep wells generally mean such as are more than 100 feet deep, but there are many considerations which qualify this definition. A deep well may be considered essentially as one the water in which has filtered through a considerable thickness of porous material, and whether the shaft of such a well is deep or shallow will depend on circumstances. If the shaft passes through a bed of clay or other impervious stratum, and the surface water above that is rigidly excluded, the well should be classed as "deep," even if the shaft is only a few feet in depth, because the water in it must have passed for a considerable distance below the clay. On the other hand, however deep the shaft of a well, it must be considered as "shallow" if water can enter the shaft near the surface, or if large cracks or fissures give free passage for surface water through the soil in which the well is sunk. With these principles in view, the water from wells may often be improved. Every care should be taken to exclude surface water from deep wells; that is to say, all water from strata within about 100 feet from the surface or above the first impervious bed. In very deep wells which pass through several such beds, it is desirable to examine the water from each group of pervious strata, as this often varies in quality, and if the supply is sufficient to exclude all but the best.

In shallow wells much may occasionally be accomplished in a similar manner by making the upper part of the shaft water-tight. It is also desirable that the surface for some distance round the well should be puddled with clay, concreted, or otherwise rendered impervious, so as to increase the thickness of the soil through which the water has to pass. Drains passing near the well should be, if possible, diverted; and of course cesspools should be either abolished, or, if that is impracticable, removed to as great a distance from the well as is possible, and in addition made perfectly water-tight. Changes such as these tend to diminish the uncertainty of the conditions attending a shallow well, but in most cases such a source of supply should, if possible, be abandoned as dangerous at best.

C.

Permanent Hardness	Sources of Supply.
—	Gathering ground in Wales on Silurian formation. 1·8 parts chalk added per 100,000.
2·7	Upland surface sources.
3·2	Deep well in South Downs.
7·1	Springs in triassic conglomerate and carboniferous limestone, also deep wells.
—	From well in the Chalk, Fulbourn.
5·3	(1) From wells in Chalk.
5·3	(2) ,, softened, as supplied to consumers.
1·5	Upland sources.
–	Springs and two deep wells (200 ft.)
14·0	N. Warwickshire Water Co.'s supply.
5·3	Wells and adits in the Chalk.
6·1	Deep chalk wells.
1-2·7	R. Exe, sand-filtered.
5·7	(1) From streams and springs, filtered through mechanical filters plus sulphate of alumina.
9·23	(2) From Upper Trias, well 250 ft. deep.
—	River water, filtered.
10·0	Wells in Chalk under Woolwich and Thanet beds.
5·1	Surface water from peaty soil resting on Millstone Grit, acid.
4·6	Deep wells in the Chalk, yielding water from the Yorkshire Wolds.
SO$_3$ 2·53	Watershed (17,000 acres) largely peat, over Millstone Grit. Daily yield (min.) 18·2 mill. galls.
—	From Derwent Valley (lime added and water mechanically filtered).
—	Lake Vyrnwy supply.
3·3	Well (100 ft.) at Bromsberrow, S. of Malvern Hills, in New Red Sandstone (Bunter).
4·3	Wells and adits in Chalk, at Wingham
0·7	Impounding reservoir on the Lune and the Balder, Tees Valley.
4·8-5·7	Stream flowing in limestone district, and moorland waters from grits and igneous rocks.
4·3	ex R. Wensum.
—	Thames above King's Weir.
·84-1·2	Rivers W. Dart, Cowsic, Blackabrook, and Meavy.
5·0	Chalk springs issuing between Chalk and Tertiary beds at Havant. Min. yield 13 mill. galls. daily.
13·3	Wells and adits in Chalk affected by sea.
	Upland surface water. Cf. Huddersfield and Leeds.
5·0	
5·0	Wells in Upper Chalk, base at surface.
10·0	ex R. Bure.
4·9	
6·8	
7·5	
4·8	
6·5	
6·7	
—	(1) Active sewage pollution going on.
—	(2) Soil filtered animal pollution in long-inhabited area. Water bacteriologically good.

[*To face p.* 498.

PART IX.

THE VOLUMETRIC ANALYSIS OF GAS.

By H. Hollings, M.Sc., A.I.C., and J. S. G. Thomas, D.Sc., A.R.C.Sc., A.I.C.

Within recent years there has been a growing tendency to control technical processes and to elucidate scientific problems by the aid of volumetric analyses of gases wherever gas samples are available, with the result that much progress in the subject has been made since the appearance of Bunsen's *Gasometry*. Compact forms of apparatus suitable for gas analysis under special conditions have been devised, and methods are available for the accurate determination of minute quantities of certain gases such as carbon monoxide. Generally, one can say that the subject is now one which will afford one or more methods for the determination of the volumetric composition of any sample of gas likely to arise in technical or research work. In some cases it is even possible to obtain an automatic record of the variation of the amount of a constituent present in a stream of gas.

Methods of Sampling.—The subject of gas analysis naturally divides itself into two parts, (1) the collection of the sample of gas and (2) the subjection of such sample to analysis. The actual collection of a sample of the gas in a sampling vessel is not in every case necessary, as in some cases a stream of gas may be continuously aspirated through, and in other cases passed directly into the gas analysis apparatus. The operation of obtaining a sample of gas is one demanding great care on the part of the operator. If the sample is to be withdrawn from a source of supply which is at a pressure greater than atmospheric, this excess pressure can itself be employed to effect the passage of the gas to the sampling vessel. Otherwise an appropriate deficit of pressure must be produced in the sampling vessel in order to effect the transference. A tube is inserted into the region containing the gas to be sampled and the gas is transferred to the sampling vessel by means of this tube. Wherever possible the tube should be of glass, which can safely be used up to a temperature of about 500° C.; above that temperature a glazed porcelain or silica tube should be employed. Iron tubes should be avoided, as iron absorbs considerable quantities of oxygen at comparatively low temperatures. Gases such as H_2S and SO_2 have an action upon various metals and the use of such metals is to be avoided. If the gas contains much dust, the end of the tube inserted into the gas should be plugged lightly with asbestos, glass wool, or cotton wool. If this is done it must be remembered that, if such a gas as crude coal gas is passed through a plug of this kind, there is a liability for certain tarry constituents of the gas to be retained by the plug and to exercise a "washing" action upon any subsequent passage of gas through the plug, thus causing the collected sample to differ from the original gas.

The sampling vessel should in general have a volume of about 100 c.c. It is essential that all tubes and vessels used for sampling should be thoroughly cleaned. The inner surfaces of tubes and sampling vessel unless thoroughly cleaned may be contaminated with substances which exercise some influence on various constituents of the gaseous mixture to be analysed, this influence being either of a chemical or physical nature. Cleansing with a strong solution of caustic soda followed by washing with distilled water and the subsequent use of a warm solution of potassium dichromate to which some strong sulphuric acid has been added constitutes a satisfactory treatment, the apparatus being finally thoroughly washed out with distilled water and dried by the passage through it of a current of dry filtered air. Rubber joints may be employed to effect the juncture of various pieces of apparatus, but care should be taken that the minimum rubber surface is exposed to the action of the gas. This can be achieved by bringing the ends of the tubes to be connected as nearly into apposition as possible, or the end of one tube may be inserted into the slightly enlarged end of the other and the joint secured by rubber tubing. Good quality rubber tubing alone should be employed, and attention given to the lubrication of all taps (see p. 509). It is advisable to remove the plugs of all taps from apparatus which is not being used.

A convenient method of sampling is illustrated in fig. 59. The end A is inserted into the gas to be sampled. By means of the three-way tap F, the portion AF is filled with mercury derived from B, the portion FE being similarly filled with mercury by opening the tap E and raising D. In lieu of the use of mercury in the part AF of the tube, which is not always convenient, B may be connected with an aspirator and the tube AF filled with the gas to be sampled, the tap F being suitably turned. D being now raised until the mercury is at F, the tap F is turned so that A is put into communication with the sampling vessel C and, by lowering D, a sample of gas is aspirated into C. Retaining C and D in their relative positions the tap E is closed, C is disconnected from the sampling tube AF and connected to the analysis vessel, to which the sample is transferred by opening E and raising D.

A very convenient modification of the method sketched in fig. 59 is shown in fig. 60. The sampling bottle A is placed on a shelf as shown and is connected with the vessel B containing mercury. Three shelves are provided for the bottles. The side tubes of the bottle A are furnished with mercury reservoirs attached to three-way taps so that the side tubes may be completely filled with mercury. The vessel B being placed on the uppermost shelf and the taps of A being appropriately opened and adjusted, mercury flows from B into A until the latter is completely filled with mercury. The taps of A are now closed and, if necessary, the side tubes completely filled with mercury from the reservoirs. To take a sample of gas, the side tube C is connected to the point from which it is to be drawn and B is removed to the lowest shelf. The taps C and D are then opened as far as necessary and a sample of gas is aspirated into the vessel A. If desired, when sampling, the rubber tubing connecting A and B may be removed and a small capillary tube, bent at right angles, attached to D.

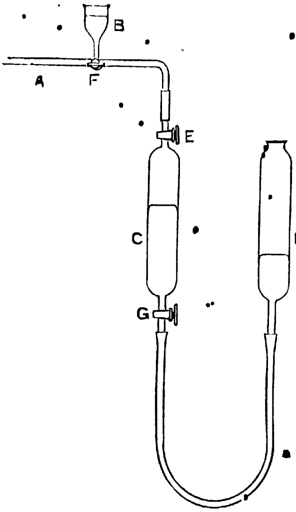

FIG. 59.

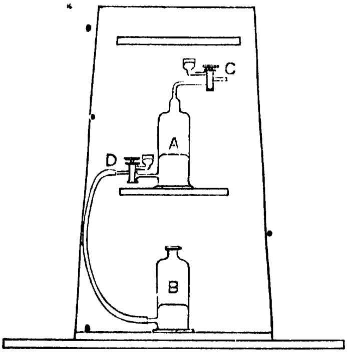

FIG. 60.

The rate of sampling is then easily controlled by regulating the rate at which drops of mercury fall from the end of this capillary.

Frequently water saturated with the gas to be sampled, or an aqueous solution of glycerin, magnesium chloride or sodium chloride is employed as the aspirating liquid in sampling vessels of the type described and with other types. The use of such liquids is not generally to be recommended as considerable variation in the percentage composition of a gaseous mixture is possible owing to the varying solubility with temperature of the different constituents of the gaseous mixture. In cases where a high degree of accuracy of analysis is essential, the most suitable liquid for use in a sampling vessel is mercury. Gray[1] has shown that ordinary industrial gaseous fuels and their products of combustion may be stored over the more concentrated aqueous solutions of glycerin or magnesium chloride without fear of any considerable change of composition, but that prolonged contact and agitation with the liquid should be avoided. It is preferable that the solution used be saturated, previous to sampling, with the gas to be sampled.

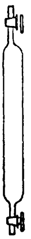

FIG. 61.

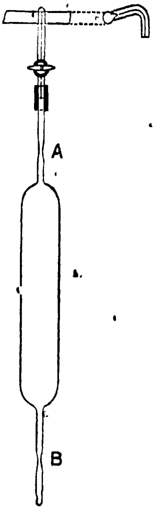

FIG. 62.

For many purposes the form of sampling vessel illustrated in fig. 61, provided with ground stop-cocks at either end is very convenient. If the stop-cocks are lubricated as described on page 509, such a sampling vessel will satisfactorily preserve a sample for a very considerable period. Occasionally, however, it is necessary to seal up a sample of gas, and the following method has been devised by Sodeau[2] (Fig. 62). The sampling vessel consists of a cylindrical bulb of about 200 c.c. capacity joined at the upper end to a narrow tube drawn down to a capillary for sealing at A and at the lower end to a tube of about 7 mm. bore drawn down for sealing at the point B about 4 or 5 cm. below the bottom of the bulb. When it is desired to collect a sample, the lower end is connected to a mercury reservoir by means of india-rubber tubing and the upper to the bent capillary side tube of a T-piece, this arrangement being adopted in order that any condensed moisture may pass straight to the aspirator instead of entering the sample vessel. After the sample has been collected, the tube is sealed at A and B in the usual manner. In order to transfer the sample, the lower tube is nicked with a glass-knife near the junction with the bulb. The end B can then be easily broken off with the fingers beneath the surface of mercury in an ordinary porcelain trough. A crucible is then slipped under the open end and the tube transferred to a mercury trough, when a capillary siphon, filled with mercury can readily be passed up through the open end of the tube and the required portion of gas drawn into the measuring tube. A single cylindrical bulb can be used many times by sealing short pieces of tubing to each of the open ends and drawing same down for sealing.

---

[1] *J. S. C. I.* 913, **32**, 1092.

[2] *Ibid.*, 1903, **22**, 190.

Frequently occasions arise for the collection of a sample of gas which shall fairly represent the average composition of the gas over a considerable period. It is clear that, in this case the rate at which the sample is collected should at any time be proportional to the quantity of gas to be sampled at that time. Arrangements can sometimes be made whereby this may be effected. When a gas sample is to be collected in the sampling vessel at a uniform rate, it is obvious that this result cannot be achieved by the forms of sampling vessels hitherto described without tedious adjustment of the tap or taps and then the adjustment can be only very approximate.

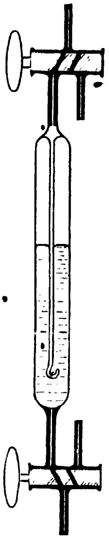

FIG. 63.

G. N. Huntly[1] has described a form of sampling vessel in which the rate of out-flow of mercury is controlled by a tap and maintained constant by a Mariotte tube through which the gas enters the sampling vessel (see fig. 63). By this means the rate at which the gas can be drawn into the vessel is maintained constant within 1 per cent. With the ordinary form of sampling vessel, the rate of sampling can be maintained constant within narrow limits by attaching to the outlet a length of tubing so that the head of outflowing liquid is thereby increased. Gray[2] has designed a very effective method for the collection of a small average sample of gas taken at a uniform rate over any specified period which may be varied at will. The device is illustrated in fig. 64. It consists essentially of an ordinary gas-sampling tube N, which may be filled with mercury from the bottle G, attached to a reservoir J which is counterpoised by a vessel R floating in water in a tank Q, the float being connected with J, by means of a cord which passes over the pulley P. The float may be a tinned iron vessel or glass bottle containing the necessary quantity of water or lead shot to establish the balance. The height of the tank must be greater than the length of the sampling tube N. The overflow tube I should be slightly longer than N and the length of the wide tube H should slightly exceed that of I. The jet V under a pressure which may be regulated by adjustment of the overflow W delivers sufficient water during the specified period to raise the level of water in the tank to a height equal to the length of the sampling tube. As the water level rises, the reservoir J is steadily lowered, so that the gas is drawn at a uniform rate into the sampling tube, and the mercury displaced escapes by way of the tube I, and is collected in G. By means of a suction pipe A, discharging into the drain pipe B, a rapid current of gas is drawn along the tube F, which is connected to the flue or gas main, a suitable filter being interposed, if necessary, to retain any solid particles. The connection O, between the sample and the tube F, is preferably made of capillary tubing 3 or 4 ins. long to prevent the diffusion of gas backwards from N to F: if desired a small non-return mercury valve may be inserted at this point. The flasks C and E, serve to indicate that the gas is passing freely along the tube F, and at the same time act as a safety valve; so long as the tube F remains clear, the gas passes through E, but if an obstruction occurs, air is drawn through the bottle C, thus preventing the pump from drawing mercury out of the sampling tube and discharging it down the drain. To start the apparatus the tube F is connected with the gas supply and a rapid current of gas is drawn through F by the filter pump. The rubber tube connecting the jet V with the water supply is then closed by the clip S and water is allowed to run into T, and to overflow freely through W, the height of which has previously been adjusted to the desired level. Water is now run from the tank Q till the top of the overflow tube I is at the level of the shoulder of the gas tube N, and J and N are now filled with mercury by raising the bottle G, after which the clip K is closed and the bottle is replaced in the position shown. The capillary O is finally filled with mercury by raising J, the lower stop cock of the sampling tube is closed and J is then lowered to its former position. The sampling tube and the capillary O are at this stage completely filled with mercury, J is filled to the overflow pipe which is level with the point where the capillary joins the shoulder of the gas tube N, and the operation of sampling may now

---

[1] *J. S. C. I.*, 1910, **29**, 312.

[2] *Ibid.*, 1913, **32**, 1093.

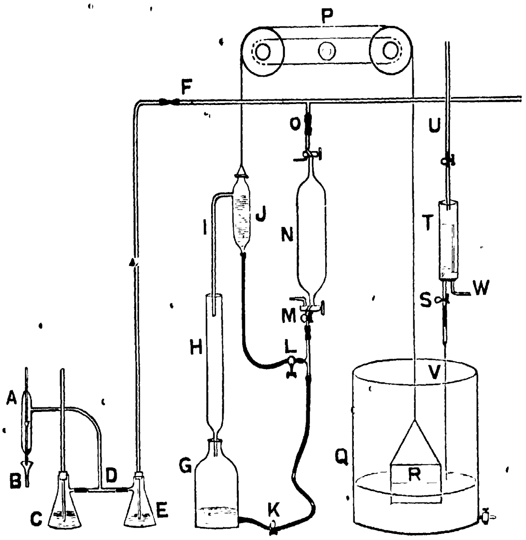

FIG. 64.

be commenced by opening the lower stop-cock of the gas tube and starting the flow of water from the jet V. By using jets of various sizes or tanks of various diameter the time of sampling may be varied within wide limits. A variation employing a clock in place of the water tank and float is also described by Gray (loc. cit.)

Purification of Mercury.—The mercury used in gas analysis—whether in the sampling vessel or in the analysis apparatus—should be carefully purified. Mercury contaminated with impurities clings to glass, and accurate readings are an impossibility under these conditions. It is desirable that all pieces of apparatus employing mercury should be set up on a wooden base having a raised edge which will serve to retain any mercury spilt during any of the operations. For convenience of collection of the mercury the base should be furnished with a small hole in one corner through which the mercury may be swept and recovered, the hole being ordinarily closed with a cork. Should the mercury become contaminated with dust, etc., the first stage in its purification consists in filtration. For this purpose a piece of hard filter paper is folded as usual and placed in a filter funnel. A small hole is then made in the apex of the filter paper by means of a pin, and the mercury poured into the filter so formed. Any dust, etc., contaminating the mercury is retained in the filter, together with a little mercury. Another good method of cleansing mercury is to put a basin underneath the middle of a piece of damp chamois leather, pour the mercury into the leather resting in the basin, gather up the sides and corners of the leather and twist them tighter and tighter until all the mercury is squeezed through the pores of the leather. The dust and dirt are retained on the upper surface of the leather. Having been subjected to the preliminary purification, the impure mercury is next subjected to the action of dilute nitric acid. The mercury is placed in the funnel A (see fig. 65) the stem of which ends in a fine jet. The mercury passes from the jet in the form of a fine spray and is subjected to the action of dilute nitric acid (1 part of conc. acid to 6 of water) contained in the glass tube B, about 1 metre long. The end of B is bent into S form as shown. The mercury in the limb C counterbalances the column of liquid in B. When sufficient mercury has collected at the bottom of B, it flows over by way of the S tube into D. The action of the apparatus is found to be more satisfactory when the discharge of mercury from the S tube is intermittent rather than continuous. When the mercury is discharged in the form of drops into D, there is a tendency for some of the solution to be carried into the S tube which ultimately becomes choked with

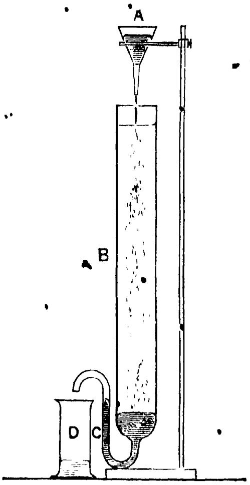

Fig. 65.

mercurous nitrate. The operation should be repeated a second time and the mercury finally passed through a column of water contained in a similar washing tower. The mercury is then dried by heating to 100° C. in an evaporating dish with constant stirring and, if necessary, is then passed through a hole in the apex of a filter paper as described above. The mercury obtained by this process of purification may be found suitable for use. If this is not the case, it is further subjected to a process of distillation under reduced pressure A form of mercury still very much employed and requiring little attention is the Clark still in which the mercury is distilled in vacuo. Mercury is liable to contamination with cadmium and zinc and, since these are volatile, distillation in vacuo does not remove them. Hulett and Minchin,[1] therefore, recommend that the distillation be carried out in a vessel in which the pressure is kept so reduced by means of a pump that a slight and controllable current of air is bubbled through the mercury during the distillation. Under these conditions, the volatile metals, cadmium, zinc, etc., form non-volatile oxides, and it is possible to obtain complete purification of the mercury from these metals. The process is carried out in an apparatus of the form shown in fig. 66. The mercury is contained in the flask A, having a long neck. To the side tube of the flask an air condenser, as shown, is sealed. The end of this condenser passes through a wooden cork into the flask B. C is a similar flask fitted with wooden cork which serves as catch vessel should water be sucked back from the filter pump serving to reduce the pressure in the system. Air in controllable amount can be bubbled through the mercury in A by means of the tube F which passes through the neck of the flask A and is drawn out to a fine capillary at its lower end. This tube is joined to the flask by a piece of rubber tubing as shown. A piece of rubber tubing which can be closed by the screw-clip E, is provided at the upper end of the tube. The flask stands on a sand bath and is surrounded by a shield of asbestos. The mercury having been introduced into A, the filter pump is started and heat applied. The

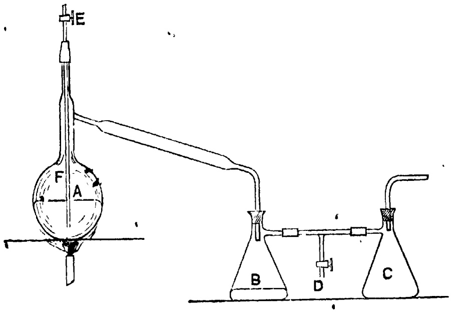

Fig. 66.

---

[1] *Physical Review*, 1905, **21**, 388.

screw clip E is so regulated that one or two bubbles of air per second pass into the mercury. Should the boiling become violent, this is checked by opening the tap D and so admitting air to the apparatus. In a little while distillation of mercury commences and the pure mercury collects in B. The method is one which has been found to yield mercury, the surface of which remains untarnished in a loosely stoppered bottle for a period of at least a year, and is to be recommended.

Mercury may also readily be prepared of sufficient purity for gas analysis purposes by placing the mercury, together with some concentrated sulphuric acid to which a little mercurous sulphate has been added, in a strong glass vessel fitted with a stop-cock through which the mercury may be drawn in a dry and clean condition as required for use. If a current of *dry* air is occasionally aspirated through the contents of the vessel, the purification process is materially hastened The air current should be drawn through a V-tube containing calcium chloride, this tube being itself permanently attached to the purification vessel.

Stop-Cocks.—Glass stop-cocks constitute an essential part of the apparatus used in gas analysis, being employed in most forms of sampling vessels and in the analysis apparatus. Various forms of stop-cock are available. In the simplest form (fig. 67) we have two leading tubes which may be connected by a hole drilled through a slightly conical plug, the leading tubes being situated diametrically opposite one another, the hole of the plug being drilled at right angles to the axis of the cone and continued into the barrel. Such a tap if well ground in and well lubricated —two desiderata frequently missing —may be used with very little fear of leakage of gas past it, even when a considerable difference of pressure is established between the inside and outside of the vessel which the stop-cock closes. The chief objection to the use of a stop-cock of such simple construction is due to the fact that in the process of grinding-in the plug, a piece of the abrasive employed may grind a small ring either in the plug or the barrel, and if such ring exist at the common level of the openings in the barrel a leak is possible from one side of the plug to the other. Such a fault is less frequently met with in stop-cocks of this construction in which the leading tubes are narrow—say of 1 mm. bore, or less—and such stop-cocks may be employed with very little risk in gas analysis apparatus. The ability of such stop-cock to prevent leakage of gas should, however, be tested from time to time. A simple test is afforded by subjecting a measured volume of air contained in a vessel closed by the stop-cock to a definite pressure, the temperature being maintained constant. Any leak is then readily detected by alteration of the level of the containing liquid in the vessel.

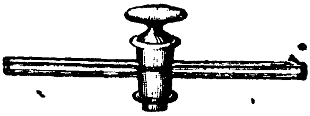

FIG. 67.

The fault just mentioned is prevented in the stop-cock of the type illustrated in fig. 68. In this the leading tubes are connected to the barrel at points situate in a diametral plane of the barrel but not at diametrically opposite points in such plane, i.e. not at the same level. The hole in the plug is bored at an inclination to the axis so that when required the leading tubes can be connected across the barrel by suitable adjustment of the plug.

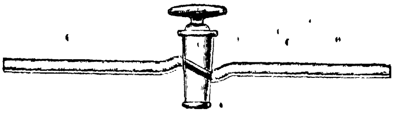

FIG. 68.

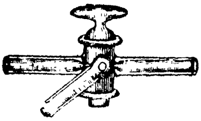

FIG. 69.

Three-way taps are of three kinds: (1) those in which the three leading tubes are situate in the same plane and in which the plug is bored in T-form (fig. 69); (2) those in which the leading tubes lie in a diametral plane of the plug, the plug being bored with two holes inclined to the axis (fig. 70); (3) those in which one leading tube is parallel to the axis of the plug (fig. 71). Of these stop-cocks it is clear that types (1) and (3) suffer from the defect already mentioned, viz. the three leading tubes being all on the same level, should a ring be ground in the plug or barrel leakage will occur past the plug. Type (1), however, possesses the

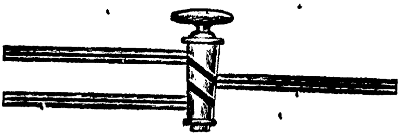

FIG. 70.

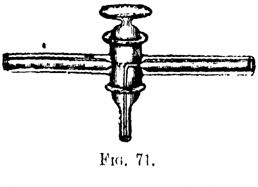

FIG. 71.

advantage that all three tubes can be put into communication at the same time, and communication can be established between any pair of tubes. The second type (fig. 70) was introduced by Greiner and Friedrich. It eliminates the defect referred to and is the most generally used. The third type is not to be recommended as the plug is liable to be loosened by motion of the other parts of the apparatus. It possesses the advantage, however, that the plug, being suitably bored, communication is possible between any pair of tubes and yet in no position of the plug are all three tubes in communication. Fig. 72 shows a three-way stop-cock provided with mercury cups, these being employed to afford additional security against leakage of gas more especially when a comparatively poor lubricant such as phosphoric acid is employed to lubricate the stop-cock.

Lubrication.—The efficient lubrication of stop-cocks is a matter requiring considerable attention. It must be remembered that it is afforded in general by a film of lubricant of thickness approaching molecular dimensions. No increased lubricating effect is produced by the indiscriminate covering of the plug with lubricant. The following lubricant is recommended by Sir Herbert Jackson: Six parts of black rubber tubing are heated with five parts of vaseline and one part of solid paraffin until the whole of the rubber dissolves, the temperature being such as to cause considerable evolution of vapour from the vaseline, while insufficient to burn the rubber. The lubricant is then allowed to cool and is applied carefully to the plug in small quantity, the plug and barrel having been previously cleaned by means of a soft duster, care being taken that no grit remains on either plug or barrel. In lubricating the plug, care should be taken to avoid closing with lubricant the hole drilled through the plug. The plug is then inserted in the barrel and turned several times, until the tap appears quite transparent and streaks are entirely absent. Especial care should be taken in the lubrication of the tap of explosion vessels. On no account must any lubricant be present in the tubes leading to the stop-cock. Any lubricant present in such position is burnt when the gaseous mixture in the vessel is exploded and the analytical result may be extremely erroneous on this account. The taps of such explosion vessels should, therefore, be lubricated with the minimum amount of lubricant very carefully applied to the plug. To avoid the possibility of error due to the cause mentioned, phosphoric acid is frequently used for the purpose of lubricating such stop-cocks.

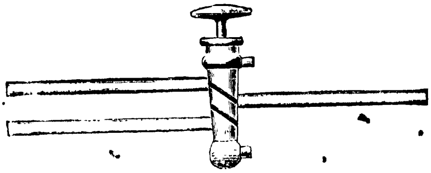

FIG. 72.

PREPARATION OF ABSORPTION AND EUDIOMETRIC TUBES WITH INSTRUCTIONS FOR ETCHING, GRADUATING, ETC.

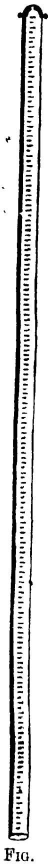

FIG. 73.

Bunsen in the various processes of gas analysis devised by him used two tubes for purposes of measurement and analysis. The tubes are known respectively as the absorption tube and the eudiometer. He generally achieved the absorption of various constituents of a gaseous mixture by means of reagents used in the form of bullets. The eudiometer differed from the absorption tube in being of greater length but measurements of volume were made in both tubes. Moreover, the eudiometer was provided with means whereby an explosion of a mixture of the gas to be analyzed along with oxygen could be effected. Although the various types of apparatus used in gas analysis have departed very considerably from the simplicity of the original Bunsen apparatus, they all make use of tubes in which various measurements of gaseous volumes are made. Such volumes can, of course, be referred to the length of tube occupied by the gas in question. The length of tube so occupied can be determined by readings taken with a cathetometer without reference to any graduations on the tube itself, and volumes so determined are probably of the highest accuracy possible. Briefly the cathetometer consists of a telescope mounted so as to be capable of motion both in a horizontal and vertical plane, its position in the latter plane being indicated by a scale. More generally, however, considerations of quickness, demand that readings of the volume shall be made by reference to a scale engraved on the tube itself. We propose, therefore, to describe in some detail the preparation of what will serve as the type of all such tubes, namely, the Bunsen eudiometer. The eudiometer has a length of from 70 to 80 cms. and a diameter of about 2 cms. and is closed at one end (see fig. 73). Into the closed end two platinum wires are sealed, so as to enable the operator to pass an electric spark through any gas which the tube may contain. The mode of sealing in the platinum wires is as follows: When the end of the tube is closed and while still hot, a finely pointed blow-pipe flame is directed against the side of the tube, at the base of the hemispherical end. When the glass is soft, a piece of white hot platinum wire is pressed against it and rapidly drawn away. By this means a small conical tube is produced. This operation is then repeated on the opposite side (fig. 74). One of the conical tubes is next cut off near to the eudiometer so as to leave a small orifice (fig. 75), through which a piece of moderately thin platinum wire, reaching about two-thirds across the tube, is passed. The fine blowpipe flame is now brought to play on the wire at the point where it enters the tube. A small piece of glass enamel is fused on to the wire and the top of the orifice through which the platinum wire is inserted, the joint is well heated, and a perfectly gas-tight joint results. The enamel serves to extend the period during which the joint remains gas-tight. If it should be observed that the tube has any tendency to collapse during the heating, it will be necessary to blow gently into the open end of the tube. This may be done conveniently by means of a long piece of rubber tubing connected to the eudiometer, the operator thus being able to watch the process more easily than if the mouth were applied directly to the tube. When a perfect fusion of the glass enamel round the wire and on the tube has been effected, the point on the opposite side is cut off, and a second wire sealed in there in the same manner (fig. 76). The end of the tube must be allowed to cool very slowly; if proper attention is not paid to this, fracture is very liable to ensue. When perfectly cold, a piece of wood with a rounded end is passed up the eudiometer and the two wires carefully pressed against the end of the tube so as to lie in contact with the glass with a gap of 1 or 2 mm. between their points (fig. 77). It is for this purpose that the wires, when sealed in, are made to reach so far across the tube. The ends of the wires projecting outside the tube are then bent into loops. These loops must be carefully treated, for, if frequently bent, they are very apt to break off close to the glass; besides this, the bending of the wire sometimes causes a minute crack in the glass which may spread and ruin the tube. These difficulties may be obviated by cutting off the wire close to the glass, and carefully smoothing the ends by rubbing them with a piece of ground glass until they are level with the surface of the tube (fig. 78). In order to make contact with the terminals of the induction coil, a wooden clip, the prongs of which are separately lined on their inner aspects with platinum foil, is made to grasp the tube in such manner that the respective pieces of foil make contact with one or other of the terminals of the platinum wire. The pieces of foil are connected each to a separate loop of strong platinum, and to these the wires from the coil are attached. Perfect

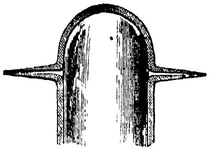
Fig. 74.

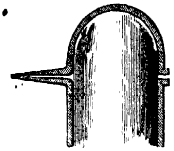
Fig. 75.

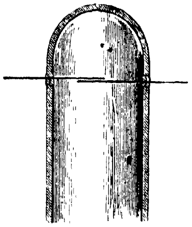
Fig. 76.

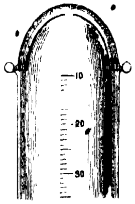

Fig. 77.

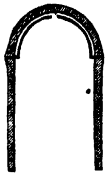
Fig. 78.

contact is thus ensured between the foil and platinum wires, and it is easy to clean the outside of the eudiometer without fear of injury to the instrument.

It will now be necessary to determine whether the glass is perfectly fused to the wires. For this purpose, the eudiometer is filled with mercury and inverted in a trough of mercury. The tube is clamped in a vertical position. If the tube is of such length that a vacuous space is left over the surface of the mercury in it, then if the position of the surface of the mercury remains constant over a period of a few minutes, the wires have been satisfactorily sealed in. If the tube is so short that when it is inverted the mercury completely fills the tube, a little air is admitted to the tube until the surface of the mercury is brought just below the level of the point at which the wires are fused in. An observation of the level of the mercury in the tube as already described will then enable one to ascertain whether the wires have been satisfactorily sealed in.

c. **Graduation of Burette.**—In the Bunsen method of gas analysis, the measurement of gaseous volume after explosion with oxygen was made in the eudiometer tube itself. In all modern forms of gas analysis apparatus, the gas, after explosion, is transferred to the so-called *burette* where volume measurements are made.

This tube is graduated in the following manner: A cork is fitted into the end of the tube, and a piece of stick, a file or anything that will make a convenient handle, is thrust securely into the cork. The tube is heated slightly throughout its whole length by being rotated and rapidly passed backwards and forwards a number of times through the hot gases from a Bunsen burner. A number of other methods whereby the tube may be heated to the required temperature—i.e. a little above the melting point of paraffin wax will present themselves, e g. the tube may be placed in a metal tube jacketed with steam or other vapour. The heated tube is then coated with melted wax by means of a camel-hair brush. Sometimes a few drops of turpentine are mixed with the wax to render it less brittle, but this is not always necessary. If, on cooling, it is found that the coating of wax is not uniform, the tube may be placed in a vertical position before a fire and slowly rotated so as to heat it evenly. The wax will then be evenly distributed on the surface of the glass, the excess flowing off. The tube must not be raised to too high a temperature, or the wax may become too thin; but all thick masses should be avoided as they may prove troublesome in the subsequent operations. In place of paraffin wax, the tube may be coated with a thin and even coating of Brunswick black diluted with benzol.

The best and most accurate method of marking the divisions on the wax is by means of a dividing engine; but the more usual procedure is to copy the graduations from another tube which has already been graduated. In some cases it is desirable to graduate the tube so that readings made thereon indicate approximately volumes in c.c., neglecting for the present the inevitable errors, which will be accounted for by subsequent calibration. In other cases the scale engraved on the tube may be a millimetre scale, etc. In either case, a hard glass tube on which appropriate divisions have already been deeply etched is fixed in a groove in the graduating table as shown in fig. 79. (When the graduation of the

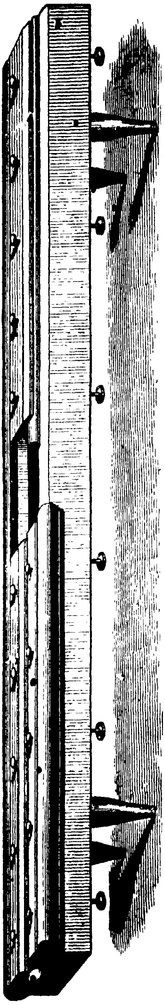

FIG. 79.

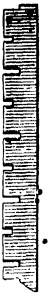

FIG. 80.

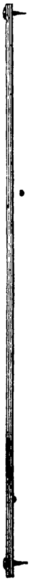

FIG. 81.

tube is to be in millimetres, a standard steel scale appropriately marked may be substituted for the hard glass tube, with advantage in the subsequent operation of graduation.) A straight edge of brass is screwed down on the tube. The waxed tube is secured at the other end of the same groove between two brass plates, the one with a straight edge, and the other with notches, appropriate to the divisions on the standard scale to be engraved, every fifth notch being slightly longer than the others as shown in fig. 80. A beam compass is constructed of a wooden rod about 3 ft. long as in fig. 81. A sharp steel point is provided near one end and a penknife blade is mounted so as to slide freely along the rod and be fixed at any desired part of the rod by means of a screw. Adjusting the penknife blade at a suitable distance from the steel point, the scale is transferred from the one tube to the waxed tube. In general, the distance between the knife blade and steel point should be made as large as convenient. The transferred graduations will be in reality small arcs of a circle of large radius, and if the radius is sufficiently large, such arcs are for all practical purposes indistinguishable from straight lines. The beam compass is held so that the steel point rests in one of the divisions of the graduated tube or scale, being gently pressed at the same time against the edge of the brass plate; the point of the knife-blade is then moved by the operator's right hand across the portion of the waxed tube which lies exposed between the two brass plates. When the line has been scratched on the wax, the point is moved along the tube until it falls into the next division; another line is now scratched on the wax, and so the process continues. At every fifth division, the knife blade will enter a notch in the brass plate making every fifth division slightly longer and every tenth division slightly longer still. After a little practice it will be found easy to transfer fifty or sixty divisions per minute and with perfect regularity. Before the tube is moved from the groove it must be carefully examined to see whether any mistake of graduation has been made. It may have happened that during the graduation the steel point slipped out of one of the divisions of the standard scale; such an occurrence is readily detected and corrected by touching the wax with a piece of heated platinum wire, after which another line is marked.[1] The tube is now removed from the groove and once more examined. If any portions of wax have been scraped off, the coating must be repaired with a hot platinum wire. Numbers have next to be etched opposite each tenth division, beginning from the closed end of the tube, the first division being marked 10, and appropriately situated with regard to the end of the tube (see fig. 77). The figures may be made with a steel pen. This has the advantage of producing a double line when the nib is pressed against the tube in making a down stroke. The date, the name of the maker, or an appropriate number should now be written on the tube.

The scale is now etched on the tube in the following manner: A piece of blotting paper is cut to a size somewhat larger in length and breadth than the scale to be engraved and is laid on the scale. The blotting paper is then moistened with hydrofluoric acid, care being taken that all air bubbles are pressed out from between the paper and the glass. The hydrofluoric acid should on no account touch the hands, and the fumes should not be inhaled. The progress of the etching process can be gauged by removing the blotting paper and scraping a portion of wax from one of the lines. If the division can be felt with the finger nail or the point of a knife the operation is finished; if not, the wax is replaced, the line restored, and the scale once more covered with the blotting paper which, if necessary, is again moistened with hydrofluoric acid.

The etching may also be effected with gaseous hydrofluoric acid, the wax tube being supported horizontally over a long, narrow, leaden trough containing sulphuric acid and powdered fluor-spar, the access of vapour to the inside of the tube being prevented by means of a cork

Whichever process of etching is employed, the tube, when sufficiently etched, is washed with water, then heated slightly and the wax wiped off with a warm cloth. Alternatively, the burette may be immersed in cold water, the wax scaling off owing to the greater contraction of the glass.

Calibration of Burette.—The burette having been graduated and etched as above, it does not follow that equal differences of readings at various parts on the scale correspond to equal volumes, as all glass tubes are liable to certain irregularities of diameter and, moreover, the graduation can never be performed without experimental error. In order to ascertain the departure from this ideal condition, the tube is subjected to a process of calibration. Briefly, this consists in ascertaining the difference in reading of a liquid meniscus when an equal volume of liquid is withdrawn from the burette at various successive parts of its length. For this purpose, the liquid employed in the calibration should be the same liquid as is subsequently to be used in the burette. In the great majority of cases, and certainly in all cases aiming at accuracy, mercury is the liquid so employed. The burette is first filled with clean mercury, care being taken that no air bubbles are entrapped between the mercury and the sides of the tube. This can be achieved by pouring the mercury into the tube in small portions at a time, inclining the tube a little and tapping the tube, when any air bubbles so entrapped will run to the surface of the mercury This process can be continued throughout the whole length of the tube until the mercury fills the burette to the required level. The burette is now set up in a vertical position and is attached to a pipette of from 2 to 5 c.c. capacity as suggested by Ostwald. (See fig. 82). The mercury is allowed to pass very slowly from the burette until it stands at the level A in the Ostwald pipette. The level of the surface of the mercury in the burette is read, the eye being placed exactly on a level with the surface of the mercury. The placing of the eye in the proper position may be ensured in two ways. A small piece of looking glass, is placed behind and in contact with the tube. The head is now placed in such a position that the reflection of the pupil of the eye is precisely on a level with the surface of the mercury in the tube, and the corresponding reading on the tube is taken. A method much to be preferred consists in viewing the surface of the mercury and the

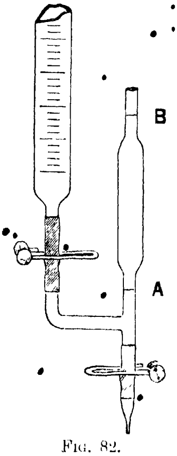

Fig. 82.

corresponding reading of the tube simultaneously by means of a cathetometer telescope. The image of the surface of the mercury is brought to the centre of the field of the telescope, indicated by the cross wires in the eye piece, and the reading taken. The telescope has the advantage of magnifying the graduations and thus facilitating the estimation by the eye of tenths of the divisions. Fig 83 represents the appearance of the tube and mercury as seen by an inverting telescope, the reading being 38·5. The mercury is now allowed to pass slowly from the burette to the pipette until the level of mercury in the latter stands at B. The tap of the burette is then closed and the volume of mercury contained between the marks A and B of the pipette delivered to a weighing bottle of known weight. The weight of the mercury is determined and its temperature noted. The operation is continued throughout the length of the burette, the weight of mercury contained in the pipette being ascertained only

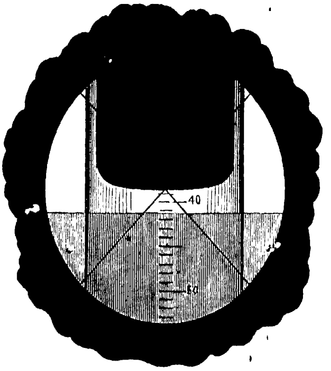

FIG. 83.

thrice during the process, viz., at the commencement, about the middle, and towards the end of the process. The last determination should not cause the level of the mercury to pass beyond the graduated portion of the scale. The temperature should not vary appreciably during the calibration. The three weighings should agree to within one part in 1000 amongst themselves, and the mean of them should be taken for purposes of calculating absolute volumes, should this be required. The volume of the mercury between the marks A and B of the pipette is

$$\frac{g\,(1 + 0{\cdot}000181\,t)}{13{\cdot}596} \text{ c.c.}$$

where t° C is the temperature of the mercury and g the weight in grammes of the mercury contained between the marks A and B of the pipette determined as above. The volume between the zero and the last calibration point is separately determined by running out the mercury until the meniscus stands at the zero mark, weighing such mercury and calculating its volume. The zero may be etched at either side of the capillary tap, but for purposes of adjustment it is best situate a little distance on the side of the tap away from the burette graduations.

We have by the process of calibration divided the tube into a number of parts each of equal volume. As an example of the method of calculation, let us assume that the following represents a series of readings obtained for successive positions of the mercury surface :—

48·2
43·1
38·0
32·8
27·7
22·7
17·5
12·4
7·3

Moreover, let the mean weight of the mercury contained between the marks A and B of the pipette, ascertained as above, be 70·04 gm. and the mean temperature 15·5° C. Also let the weight of mercury contained between the mark 7·3 and the zero be 99·42 gm. and the temperature 15·7° C. Then the volume from the zero to the graduation 7·3

$$= \frac{99{\cdot}42\,(1 + {\cdot}000181 \times 15{\cdot}7)}{13{\cdot}596} = 7{\cdot}33 \text{ c.c.}$$

The standard volume run out by means of the pipette is, in like manner,

$$\frac{70{\cdot}04\,(1 + {\cdot}000181 \times 15{\cdot}5)}{13{\cdot}596} = 5{\cdot}17 \text{ c.c.}$$

We are now able to construct the following table:—

Reading of Burette.	Corresponding Volume c.c.
7·3	7·33
12·4	7·33 + 5·17 = 12·50
17·5	12·50 + 5·17 = 17·67
22·7	17·67 + 5·17 = 22·84
27·7	22·84 + 5·17 = 28·01
32·8	28·01 + 5·17 = 33·18
38·0	33·18 + 5·17 = 38·35
43·1	38·35 + 5·17 = 43·52
48·2	43·52 + 5·17 = 48·69

A correction has to be introduced owing to the fact that during the process of calibration the concavity of the meniscus is turned towards the tap of the burette while when used in gas analysis, the concavity is directed away from the tap. A little consideration (see figs. 84 and 85) will at once enable one to see that the actual volume of gas enclosed between the tap and the surface of the mercury corresponding to any given reading, say ten, is greater under the actual conditions of use than is the case under the conditions of calibration. If water is used in the burette for analysis and calibration purposes, the meniscus is concave upwards and the correction instead of being additive, as in the case of mercury, is subtractive. The correction necessary on account of such curvature is known as the *meniscus correction*. Its value has been ascertained by Bunsen[1] for tubes of various diameter. Winkler[2] has determined the value of the correction for mercury and water, and is of opinion that Bunsen's corrections are too low. Subsequent investigations by Göckel[3] indicate that Bunsen's figures are substantially correct, although this view is controverted by Winkler in a subsequent paper.[4] Values for the meniscus correction have also been given by Geppert,[5] who found higher values for wet mercury than was the case with dry mercury. The following table gives what may be called the double meniscus correction, as determined by Göckel for water and mercury:—

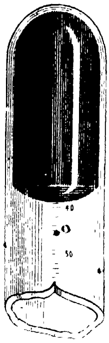

FIG. 84.

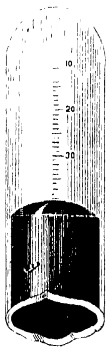

FIG. 85.

---

[1] *Gasometrische Methoden*, 2nd Edition, p. 38.

[2] *Zeit. anal. Chem.*, 1901, **40**, 403.

[3] *Zeit. ang. Chem.*, 1903, **16**, 49.

[4] *Ibid.*, 718.

[5] *Die Gasanalyse und ihre physiologische Anwendung*, 1885.

Diameter of Tube.	Double Meniscus Correction c.c.	
mm.	Mercury.	Water
1	·0026	·0021
2	·0052	·0043
3	·0090	·0093
4	·0128	·0144
5	·0200	·026
6	·027	·039
7	·035	·062
8	·043	·084
9	·056	·114
10	·068	·144
11	·080	·190
12	·091	·236
13	·104	·263
14	·118	·291
15	·140	·343
16	·162	·395
17	·174	·443
18	·185	·492
19	·181	·520
20	·177	·548
21	·180	·605
22	·182	·663
23	·179	·708
24	·176	·754
25	·176	·800

Assuming then that our burette has a diameter of 1·8 cm. we see that the previous table has to be corrected by the addition of 0·19 c.c. to each of the values in the second column. The table so amended appears as follows:—

Reading of Meniscus.	Corresponding Volume c.c.
7·3	7·52
12·4	12·69
17·5	17·86
22·7	23·03
27·7	28·20
32·8	33·37
38·0	38·54
43·1	43·71
48·2	48·88

A meniscus correction should also be introduced correcting for the curvature of the mercury surface when at the zero. As, however, this zero is situate in general in a capillary tube its magnitude is small and usually neglected.

The correct reading of volume can now be ascertained at each division of the scale, thus: between 7·3 and 12·4, a difference of scale reading of 12·4 - 7·3, i.e. 5·1 corresponds to a volume difference = 12·69 - 7 52 = 5·17. One scale division therefore corresponds to a volume difference $\frac{5·17}{5·1}$ = 1·014 c.c. The difference for 0·3 division at this part of the scale is therefore easily obtained as 0·30. The difference for 0·7 division is seen to be 0·71.

In this manner the final calibration table is calculated as below:—

Reading.	Volume.	Reading.	Volume.	Reading.	Volume.
7	7·22	21	21·33	35	35·55
8	8·23	22	22·32	36	36 55
9	9·24	23	23·35	37	37·54
10	10·26	24	24·39	38	38·54
11	11·27	25	25·42	39	39·55
12	12·29	26	26·46	40	40·57
13	13·30	27	27·50	41	41·58
14	14·31	28	28·51	42	42·60
15	15·33	29	29·53	43	43·61
16	16·34	30	30·54	44	44·62
17	17·36	31	31·56	45	45·64
18	18·35	32	32·57	46	46·65
19	19·34	33	33·56	47	47 67
20	20·34	34	34·56	48	48·68

The volume between any two graduations is now obtained by reference to the calibration table. The correction for expansion of the glass is very rarely applied, as it is negligible. The temperature of calibration should be recorded thus, e.g. $\frac{15·5°}{4°}$, indicating that the calibration was carried out at 15·5° C. and that volumes are expressed in terms of the volume of 1 gm. of water at 4° C.

CORRECTION OF VOLUME OF GAS FOR TEMPERATURE AND PRESSURE.

As is well known, the volume of a gas is dependent upon its temperature and the pressure to which it is subjected, and in every case when a gaseous volume is measured the observed volume must be reduced to the corresponding value under what are regarded as normal conditions of temperature and pressure. The most generally employed normal temperature is 0° C., and the most generally employed pressure, one due to a column of mercury 760 mm. in height and of density 13·596. The variation of the density of mercury over the range from 0° C. to 30° C. is 0·0738, thus an error of about 0·5 per cent. would be introduced by a variation in temperature of 30° C. in the temperature of the barometer. The reduction of the height of the barometric column to 0° C. is generally omitted in gas analysis, but is necessary when an accuracy of 0·1 per cent. or so is aimed at in the analysis. If the percentage composition of a gaseous mixture is to be expressed to the second place of decimals—indeed if the predominant components are to be expressed to one significant decimal place—the barometric height ought, throughout the analysis, to be reduced to the standard temperature of 0° C. The necessary correction is made by employing the appropriate value of the density of mercury given in the Appendix, Table 2. The necessary formula is $H_0 = H\{1 - (\beta - \alpha)t\}$ where H = height of barometer at $t°$, H_0 = reduced height at 0° C., β = coefficient of cubical expansion of mercury and α = coefficient of expansion of material of the barometer scale.

When comparative volumes only are required, a pressure of 1000 mm. of mercury is frequently employed as standard pressure. The calculation is thereby somewhat simplified but the procedure is not to be recommended. Frequently in technical practice the standard conditions of temperature and pressure are specified as 60° F. and a pressure represented by a column of mercury 30 ins. in height, the gas being saturated with water vapour. In some cases a temperature of 15° C. is taken as standard temperature. In technical practice the reduction of gaseous volumes to equivalent volumes under normal conditions of temperature and pressure is quickly effected by employing what is known as the tabular number. Such tabular number is calculated in the manner detailed below and represents the volume occupied under standard conditions by a mass of gas which under experimental conditions occupies unit volume. Applying the Laws of Gases associated with the names of Boyle and Charles the necessary corrections are easily deduced as follows:—

Let V = observed volume at $t°$ C.

V_0 = the reading corrected to 0° C. and 760 mm. of mercury.

B = barometer height in mm. of mercury (corrected for temperature if necessary as already explained) at time of experiment.

h = deficit of pressure in burette from atmospheric in mm. of mercury. (There is a *deficit* of pressure in the burette when the mercury level in the burette is above the level of the mercury surface in contact with the atmosphere.)

T = the vapour pressure of water expressed in mm. of mercury, at temperature $t°$ C.

(For values of T see Appendix, Table 1.)

Then $V_0 = \dfrac{V \times (B - T)}{(1 + 0{\cdot}003665\,t)760}$ if the gas is saturated with water vapour at $t°$ C.

and $V_0 = \dfrac{VB}{(1 + 0{\cdot}003665\,t)760}$ if the gas is dry.

For facilitating calculation, values of $1 + 0{\cdot}003665t$ and of the logarithm of same are given in Appendix, Table 3, and a series of tabular numbers enabling measured volume of moist gas to be readily reduced to standard conditions represented by 60° F. and 30 ins. of mercury are given in Appendix, Table 4.

When the estimations are made rapidly and comparative values only are required it is customary to omit this correction for temperature and pressure, provided no appreciable variations have occurred during the progress of the analysis. In this connection it may be mentioned that a variation of 7 mm. in pressure or of 3° C. in temperature introduces an error of the order of 1 per cent. in the percentage analysis of the gas. The variation in gaseous pressure is not entirely due to a variation of atmospheric pressure but—except where the analysis is done at constant pressure—is necessarily introduced by any variation in the height of the mercury meniscus in the burette above the free surface of the mercury in contact with the atmosphere.

Automatic Correction for Temperature and Pressure.—The correction of gaseous volumes for temperature and pressure, as explained, involves a certain amount of calculation, and numerous devices have been introduced for the reduction of the necessary calculation and in many cases the complete elimination of calculation altogether. Amongst devices of the former class may be mentioned that described by Winkler based upon the method originated by Williamson and Russell[1] of always measuring the volume of the gas at the same elasticity. A tube about a metre long is closed at one end and graduated up to 120 c.c. in tenths of a c.c. A few drops of water are poured into the tube and mercury then poured in, so that the volume of air enclosed by the tube when inverted over mercury is about 100 c.c. The actual volume of air under the observed conditions which at 0° C. and under a pressure of 760 mm. pressure would occupy a volume of 100 c.c. is now calculated by the formula

$$V = \frac{(760 - 4{\cdot}6)\,100\,(1 + 0{\cdot}003665\,t)}{B - T}$$

where $4{\cdot}6$ = pressure of water vapour at 0° C. in mm. of mercury.
t = observed temperature in °C.
B = observed barometric pressure.
T = pressure of water vapour at t° C. in mm. of mercury.

Air is now carefully introduced into the tube until, when the mercury is at the same level inside and outside the tube, the mercury stands exactly so that the air in the tube occupies the calculated volume V. This tube is now allowed to stand alongside the burette of the gas analysis apparatus in the jacket containing the burette, and the level of mercury so adjusted that equal pressure exists in each tube. If then

V_0 = volume of gas in subsidiary tube under standard conditions
V_0^1 = ,, ,, ,, ,, ,, ,, ,, actual conditions
V_1 = ,, ,, ,, ,, burette ,, ,, standard conditions
V_1^1 = ,, ,, ,, ,, ,, ,, ,, actual conditions

Then clearly $V_0 : V_0^1 = V_1 : V_1^1$.

Hence $$V_1 = \frac{V_0 \times V_1^1}{V_0^1} = 100\,\frac{V_1^1}{V_0^1}.$$

A similar method of correction can of course be employed when the gas is dry, no water being in this case introduced into the subsidiary tube and the preliminary calculation of V being made by the formula

$$V = \frac{760 \times 100 \times (1 + 0{\cdot}003665\,t)}{B}.$$

---

[1] *Proc. Roy. Soc.*, **9**, 218.

The comparison tube and the burette should, for preference, be set up in a wide tube filled with water. The adjustment of pressures and the readings of volumes should if possible be made by means of a cathetometer, whereby parallax error is eliminated and variation of temperature of the gas reduced to a minimum.

The "Kew Principle" Correction Tube.—The method is designated "Kew Principle" because, as in the Kew pattern barometer, the disturbances of level of the water are allowed for in the graduation of the instrument. This method of correction is employed in Sodeau's[1] Gas Analysis apparatus (see p. 558). The tube (represented in fig. 102) consists of a cylindrical bulb of capacity considerably exceeding 50 c.c., sealed at its upper end to a small stop-cock and at its lower end to a U-tube of which the descending limb is graduated in $\frac{1}{20}$ c.c., while the ascending limb has a marked increase of diameter at a level corresponding to that occupied by the graduations of the other limb. The outer end of the stop-cock is attached to a bent-glass tube terminating in a short length of rubber tubing. After cleaning, the apparatus is fixed in the water jacket along with the measuring burette. The stop-cock is opened and water introduced until the lower part of the meniscus corresponds with the zero of the graduations, the adjustment being easily achieved by pinching the short length of rubber tubing. The instrument then requires no further attention until the water has been sensibly reduced by evaporation, except the momentary opening and closing of the stop-cock immediately before an analysis is commenced so that the water may be brought approximately to the zero and large correction numbers avoided. Readings may be taken by means of a telescope or lens of about 5 ins. focus. The volume of air, x, enclosed in the bulb and above the zero mark is such that the water is displaced one scale division by changes of temperature and pressure causing the gas to alter in volume by 0·1 per cent. A small division has a volume of 0·05 c.c. so that the changes of temperature and pressure necessitating 1 per cent. correction of volume is accompanied by 0·5 c.c. displacement of water. If the difference of water level is thereupon changed by N mm. we have

$$1{\cdot}01\,x\,(760 \times 13{\cdot}6) = (x + 0{\cdot}5)\{(760 \times 13{\cdot}6) + \mathrm{N}\}$$

giving $$x = 50 + \frac{101\,\mathrm{N}}{206{\cdot}7 - 2\mathrm{N}}$$ [2], very approximately.

The value of N can easily be ascertained from the respective diameters d_1 mm. and d_2 mm. of the two limbs of the U-tube. Thus, if a displacement of 0·5 c.c. of water means a descent of h_1 mm. in one limb and an ascent of h_2 mm. in the other we have, evidently,

$$h_1 + h_2 = \mathrm{N} \quad (1),$$

and $$\frac{\pi d_1^2 h_1}{4} = \frac{\pi d_2^2 h_2}{4} = 500 \ (2)\ ;$$ as 0·5 c.c. = 500 c.mm.

---

[1] *J. S. C. I.*, 1903, **22**, 187.

[2] This formula differs slightly from that given by Sodeau, who used the value 13·5 for the density of mercury whereas we have used the value 13·6.

From (1) and (2) we have

$$\frac{2000}{\pi d_1^2} + \frac{2000}{\pi d_2^2} = \mathrm{N}.$$

If $d_1 = 6·9$ mm. and $d_2 = 15·5$ mm., this gives $\mathrm{N} = 13·35 + 2·65 = 16·0$. The corresponding value of v is found from the relation above to be

$$v = 50 + \frac{101 \times 16·0}{206·7 - 32·0} = 59·2 \text{ c.c.}$$

The zero being so adjusted that the total volume of the bulb together with the portion of the tube above the zero has the value of 59·2 c.c., the necessary percentage correction of volume in order to reduce the volume of gas in the burette to standard conditions is read off directly on the scale as easily as temperatures are read on a thermometer.

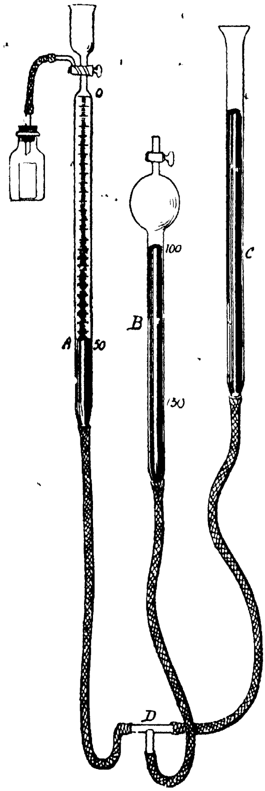

FIG. 86.

The two methods described necessitate some little calculation in order that the appropriate correction for temperature may be applied, but such correction is easily ascertained. Many devices, have, however, been introduced whereby the necessity for any calculation whatsoever is entirely eliminated. Of such devices we will describe the following:—

Lunge's Gas-Volumeter.[1]—This device was introduced by Lunge more particularly for use in cases where the gas to be measured is evolved from a weighed quantity of a liquid or solid. It is capable, however, of very general application. The apparatus is illustrated in fig. 86. A is the vessel in which the volume of gas is measured: it may be any form of nitrometer, or any convenient burette. B is the reduction tube which has at its upper end a spherical or cylindrical bulb. The volume to the first mark is 100 c.c., the remaining narrow portion of the tube being calibrated up to 130-140 c.c. in divisions representing $^1/_{10}$ c.c. This reduction tube is set once for all at the beginning of the work, by observing the thermometer and barometer, and calculating the volume which 100 c.c. of dry (or moist) air would occupy under these conditions. This calculation is made as already explained, the necessary volumes for dry and moist gases being given by

---

[1] *Z. angew. C.*, 1890, 139-144; *J. S. C. I.*, 1890, 9, 547.

$$V = \frac{100\,(273 + t)\,760}{273 \times P} \text{ for dry gases } \quad . \quad . \quad . \quad (1)$$

and

$$V = \frac{100\,(273 + t)\,760}{273 \times (P - p)} \text{ for moist gases } \quad . \quad . \quad . \quad (2)$$

where t° C. is the temperature measured, P the atmospheric pressure and p the vapour pressure in mms. of mercury of water at t° C. The volume V in (2) is the volume of moist gas measured under conditions of temperature and atmospheric pressure represented by t° and P respectively which would occupy at 0° C. and under a pressure of 760 mm. of mercury a volume of 100 c.c., *the gas at this standard temperature being quite dry.* If the gas is to be taken as *moist* under standard conditions, then the appropriate value of V is

$$V = \frac{100\,(273 + t)\,(760 - 4{\cdot}6)}{273\,(P - p)}.$$

This volume of air (together with a few drops of water if moist gases are in question or a drop of sulphuric acid if the gases are to be measured dry) is admitted into B by opening the stop-cock and raising or lowering C until the mercury in B stands at the appropriate level in B, determined as above. The stop-cock on B is then closed. A and B may, if necessary, be surrounded with water jackets. When a volume of gas is enclosed in A, the volume of such gas under standard conditions is determined as follows: The three tubes A, B and C are so adjusted that the mercury levels in A and B are the same, C being raised or lowered until the mercury level in B stands at the mark 100 c.c. It is clear that under these conditions the gases in A and B are under the same conditions of pressure and temperature (suitable precautions being taken to ensure equality of temperature), and, moreover, since the gas in B has been adjusted to the volume it would occupy under standard conditions it follows that the volume of gas in A is the volume it would occupy under such standard conditions. Frequently the volumeter is employed in such manner that the tube A contains caustic potash as well as mercury. In this case the compensation for temperature and pressure is effected as explained, save that on the reduction tube B a fiducial line is made at a distance below the 100 c.c. mark equal to the result obtained by multiplying the length of the column of caustic potash by the ratio of the specific gravity of mercury to that of the caustic potash solution (about 10). The mercury level in B is then adjusted to 100 and the mercury level in A adjusted to equality with this fiducial line. Under these conditions it is clear that the gases in B and A are under identical conditions of pressure, the pressure of the column of potash (or other liquid in other cases) being counter-balanced by the pressure of the column of mercury between the 100 c.c. mark and the fiducial line. The graduation of A, in cases where the apparatus is invariably employed in connection with the measurement of a gas of fixed composition (pure or a mixture of fixed percentage composition), can be made so as to read directly in milligrams.

The following arrangement illustrated in fig. 87 for compensating for alterations in pressure and temperature has been introduced by **Levy**.[1] The device is a slight modification of Haldane's control tube described below. The absorption pipette A has the form shown and communicates with the compensating tube C *via* the vent cock B. This is similar in shape and equal in capacity to the measuring burette D. The reservoir E is attached to the pipette by rubber tubing. At the commencement of an analysis, the liquid levels in the capillary tubes are adjusted to the marks F and G, and the vent cock B is closed to the atmosphere. After making an absorption, the mercury level in the burette D is adjusted so that the level of the absorbing liquid is returned to the mark F. Should any change in barometric pressure or temperature have occurred, the volume of air in the compensating tube C will have altered and the level of liquid will be displaced from G. The reservoir E is raised or lowered until the volume of air returns to its former value as indicated by the level of the absorbing liquid standing at G in the compensating tube. This manipulation affects equally the gas in the burette, and the level of the absorbing liquid is returned to F by slight readjustment of the mercury level in the burette. External variations are thus entirely compensated for and the readings are reduced to the values corresponding to the initial conditions of temperature and pressure. It may be noted that the adjustment is made by an observation of the level of the absorbing liquid and can, therefore, be made more accurately than would be the case if the adjustment were determined by the observation of the level of a mercury surface.

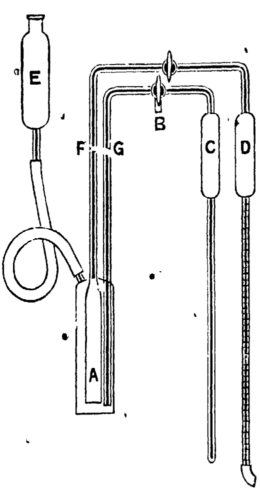

Fig. 87.

Hempel's compensating device is illustrated in fig. 88 and is intended for use with a constant-pressure form of gas analysis apparatus. A correction tube B is connected with the burette A *via* the U-tube C. If the measurements of gas volumes in A are to be made on moist gas, a drop of water is introduced into the gas in B. The adjustment to constant pressure of the gas contained in A is secured by adjusting the level in the mercury reservoir connected to A, so that equality of level of the mercury contained in the U-tube results. The pressure in A is thus always adjusted to equality with the pressure in B. The device has been improved by **Edwards**[2] who has introduced modifications which make manipulation very much easier and add to the accuracy of adjustment possible. As shown in fig. 89, the capillary from the three-way cock E on the burette is kept very long and bent over to dip into a tube C of rather large bore. In this manner, the equivalent of a U-tube having one limb of large diameter and one of small diameter is obtained. Practically the whole movement of liquid consequent on variation in pressure takes place in the capillary which is of about 1 mm. diameter. A 5 per cent. solution of sulphuric acid tinted with methyl orange is used as the confining liquid. The side connection to the correction tube is made as high as possible in order to avoid a large waste space above the level of the liquid. If the thread of liquid in the capillary breaks at any time, it is reformed by expelling with air and allowing the liquid to run back. Atmospheric pressure can be secured in the correction tube B, when necessary, by opening the tap D temporarily, and adjustment to equality of pressure in A and B is achieved by equality of level of the liquid in the capillary and the wider tube of C.

---

[1] *Journal of Gas Lighting*, 1913, 122, 526.

[2] *Ibid.*

Haldane's compensating device[1] is represented diagrammatically

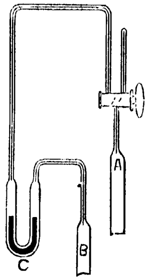

Fig. 88.

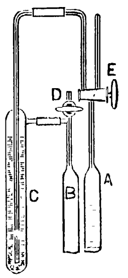

Fig. 89.

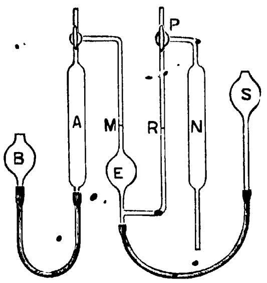

Fig. 90.

in fig. 90 and is employed in his well-known apparatus for air-analysis. When determining small quantities of gases in gaseous mixtures, variations of temperature and pressure during the analysis, unless allowed for, may cause considerable errors. A is the burette in which the measurements of volume are made, the level of mercury in A being adjustable by raising or lowering the mercury reservoir B. The compensating device proper is composed of the portions E, N and S with the accompanying glass connections. N is the compensating tube, sealed at the bottom, and containing a trace of water, and in the apparatus as actually employed is placed along with the measuring burette A in a water jacket so that differences of temperature between A and N are eliminated. X and P are three-way taps. E is the absorption pipette. The tube of the absorption pipette E and the tube R are provided with reference marks, as shown, for adjusting the pressure. Before making an absorption, N is first put in communication with R and the reservoir S which contains the absorbing solution is raised or lowered until the liquid level stands at the reference mark R. The volume in A is to be measured under the atmospheric pressure existent at the commencement of the analysis and this is ensured by the absorbing liquid in E standing at the reference mark engraved on the tube M. It is clear that this procedure ensures that the volumes of gas in A and N are subjected to the same conditions of temperature and pressure and that these conditions are entirely determined by the volume of the gas in N. If, therefore, throughout the analysis, adjustment of the volume of the gas in N is made so that the level of the surface of the confining solution is at the reference mark on R, then it follows that volume readings of the gas in A are made under conditions equivalent to those reigning when the initial adjustment of volume in N was made. Under these conditions, variations of pressure and temperature occurring during the course of an analysis are entirely compensated for, so far as their effect on the readings of volume of the gas in A is concerned.

---

[1] *Ventilation of Factories and Workshops, Blue Book* (*Cd.* 1302), 1903. *Appendix.* Haldane, *Methods of Air Analysis*, 1918, p. 14.

THE VALUES OF THE PHYSICAL CONSTANTS OF CERTAIN GASES.

For purposes of gas analysis, it is convenient to have handy reference tables of the values of certain physical characteristics of the various gases.

The values of such physical characteristics as the weight per litre of dry gas at 0° C. and 760 mm. pressure, the solubility of the gas in water at 15° C., etc., are of importance and a number of such data are collected together in Table A (see p. 599).

The solubility of air in water is, of course, conditioned by the different solubilities of its constituents. As seen from the Table A, the solubility of nitrogen in water is about half that of oxygen, whereas the partial pressure of the nitrogen in the atmosphere is approximately four times that of the oxygen. The following table gives the respective volumes of nitrogen and oxygen, contained in air, dissolved by 1000 c.c of water when saturated with air at 760 mm. pressure, the volume of gas being throughout measured at 0° C. and 760 mm.

Constituent of Air	Temperature of Water.				
	0° C.	10 C°.	15° C.	20° C.	30° C.
Nitrogen	19·0	15·0	13·5	12·3	10·4
Oxygen	10·2	7·9	7·0	6·4	5·3
Total volume dissolved	29·2	22·9	20·5	18·7	15·7
Per cent. of nitrogen by volume in dissolved air	65·1	65·5	65·9	65·8	66·2

Nitrogen peroxide N_2O_4 dissociates into $2NO_2$ as its temperature is raised. The balanced dissociation $N_2O_4 \rightleftharpoons 2NO_2$ proceeds more and more towards completion in the direction indicated by the upper arrow as the temperature is raised. The degree of dissociation into molecules having molecular formula NO_2 is conditioned also by the pressure to which the gas is subjected. The following table gives the observed values of the density of the gas relative to oxygen (0 = 16) at 0° C. and 760 mm. pressure, in latitude 45°. (See *Physical and Chemical Constants,* Kaye and Laby, p. 26, also *Recueil de Constantes Physiques, Société Française de Physique*, p. 168.)

Temperature °C.	Density 0 = 16.
26·7	38·37
39·8	35 62
60·2	30·12
80·6	26 06
100·1	24·33
121·5	23·46
154.0	22·88
183·2	22 73

The normal density of N_2O_4, in the absence of any dissociation, at 0° C. and 760 mm. pressure, relative to 0 = 16 would be 46·00.

METHODS OF ANALYSIS.

Having described some of the preliminary operations and having reviewed the principles underlying the technique of gas analysis we are now in a position to examine the methods employed ; these may be classified as follows :—

1. **Direct Absorption.**—Some gases are determined by direct absorption by certain reagents, the diminution of the volume indicating the quantity of the gas present.

2. **Indirect Determination by Explosion.** — Combustible gases are often determined by explosion, or by combustion at a high temperature, with excess of air or oxygen, and the components are determined from the diminution in volume after explosion, the quantity of carbon dioxide formed (as determined by absorption) and the quantity of oxygen consumed as determined by absorption of the residual oxygen.

Oxygen may be determined by explosion with excess of hydrogen when other combustible gases are absent.

3. **Fractional Combustion.** -- Certain gases can be determined by fractional combustion using an oxidizing agent with or without a catalyst at a carefully controlled temperature.

4. **Micro-Analysis.**—The above methods are not generally applicable when it is desired to determine gases present to the extent of, say, 0·2 per cent. or less in gaseous mixtures, and special methods giving a high degree of accuracy have been devised to meet such cases.

5. **Special Methods.**—A few gases are most accurately determined by methods which do not come within the above classification and which require separate treatment. There are also many cases in which particular devices are used in specific technical analyses. The more important of these are noted towards the end of this section.

DIRECT DETERMINATION BY ABSORPTION.

BUNSEN, who was the pioneer worker in the field of gas analysis, worked with a simple absorption tube or eudiometer and absorbed the various gases by means of solid reagents fashioned into bullets attached to a platinum wire. In some cases a suitable solid medium was impregnated with a liquid reagent. Such methods are now quite obsolete, but details may be found in Bunsen's *Gasometry*. Solid reagents may be recommended for use in a few special cases, particularly for the absorption of impurities in the preparation of pure gases.

In all modern gas analysis apparatus those gases which admit of direct absorption are brought into intimate contact with liquid or dissolved reagents contained in a vessel separate from, but having connection with, the measuring vessel.

The different absorbents used for the various gases are given below.

Acetylene is absorbed in an ammoniacal solution of silver chloride prepared by saturating pure concentrated ammonia (sp. gr. 0·880) with silver chloride freshly precipitated from the nitrate. The ammonia left in the gas after this absorption, is removed by dilute sulphuric acid before any measurement is made.

Ammonia should be determined by titration if a sufficiently large sample of gas can possibly be obtained. If, however, a small sample only is available, the ammonia may be absorbed in a 10 per cent. solution of sulphuric acid, but considerable care is necessary owing to the readiness with which the gas is absorbed by any trace of moisture in any part of the apparatus. Furthermore, the solubility of other gases (e.g. CO_2) in the 10 per cent. acid is appreciable and may cause a high result unless the absorption is carried out quickly and with a small volume of solution.

Benzene is readily absorbed by concentrated sulphuric acid (which must contain 95 to 97 per cent. H_2SO_4). This reagent also absorbs propylene and the higher olefines (but not ethylene) if they are present (see below) The presence of higher olefines in the gas is indicated by the acid turning brown. Some workers recommend the use of fuming sulphuric acid (containing about 10 per cent. free SO_3) for the absorption of benzene and olefines, followed by absorption of SO_3 by caustic potash, but if other hydrocarbons are present it will be found that the use of ordinary sulphuric acid as above will give more reliable results.

If it is not necessary to differentiate between benzene and ethylene, both may be absorbed together in a solution of bromine in normal potassium bromide solution. The bromine remaining in the gas after this treatment is removed by absorption in caustic soda or caustic potash before any measurement is made.

Dennis and M'Carthy[1] recommend the use of an ammoniacal solution of nickel cyanide for the absorption of benzene.

The use of sulphuric acid as an absorbent is preferred when dealing with complex gas mixtures such as coal gas, because it can be used at an early stage of the analysis before any of the benzene has been dissolved.

---

[1] *J. A. C. S.*, 1908.

For special methods of determination see p. 578.

Carbon Dioxide is readily absorbed in aqueous solutions of caustic soda or caustic potash, and a high degree of accuracy is possible if care has been taken that none of the gas has been lost by absorption in other reagents before this stage of the analysis is reached. When the cost is not prohibitive, KOH should be used in preference to NaOH owing to the higher solubility of the carbonate formed. If KOH is used it should be made up to a 33 per cent. solution ; NaOH should be made up to a 25 per cent. solution.

See p. 598 for special methods of determining carbon dioxide.

Carbon Monoxide is absorbed in an ammoniacal solution of cuprous chloride. To prepare this solution 75 gm. of cuprous chloride are added to a solution of 15 gm. of ammonium chloride in 80 c.c. of water and then concentrated ammonia is added until solution is complete. The solution should be kept in contact with copper wire or turnings in a stoppered bottle.

The absorption of carbon monoxide by this solution is slow, and intimate contact between gas and liquid is necessary. If the gas under examination contains more than 10 per cent. CO it should be treated a second time with a fresh solution, but care must be taken to avoid the use of excessive volumes of solution owing to the solubility of other gases, e.g. methane After the absorption, ammonia must be removed from the gas before any measurement is made.

Several different formulæ for making up the cuprous chloride solution have been suggested, but the above solution will be found satisfactory in apparatus where a little fresh solution can be taken for each absorption. A convenient solution (containing less free ammonia) for use in Hempel pipettes or apparatus of the Orsat type is made up by adding 125 c.c. concentrated hydrochloric acid to 40 gm. cuprous chloride in an 8 oz. flask ; 130 c.c concentrated ammonia are then added slowly, the flask being cooled to atmospheric temperature. A little more ammonia (about 15 c.c.) is then added until the white precipitate just dissolves ; a few drops of concentrated hydrochloric acid may be added if the solution smells of ammonia.

Some workers recommend an acid solution of cuprous chloride, but this cannot be used in contact with mercury. Furthermore, Drehschmidt[1] has shown that after prolonged use the acid solution is a less efficient absorbent than the ammoniacal solution.

Ethane and the higher paraffins should be determined indirectly by explosion, but in special cases they may be estimated approximately by absorption in absolute alcohol, water being used for the removal of alcohol vapour.

Ethylene is absorbed by an aqueous solution of bromine (water half saturated with bromine) or by a saturated solution of bromine in normal potassium bromide. Propylene and the higher olefines are simultaneously absorbed if they have not been removed previously with the benzene. Taplay[2] states that if the aqueous solution of bromine is employed, the olefines may be separated from benzene, whereas the potassium bromide solution absorbs benzene.

---

[1] *Ber.*, 1887, **20**, 2752 and 1888, **21**, 2158.

[2] *J. Gas Lighting*, 1913, **124**, 870.

Fuming nitric acid may be used as an absorbent for benzene and olefines if carbon monoxide is absent.

Hydrochloric Acid and the other halogen acids should be determined by titration. Bunsen absorbed these gases by means of solid sodium phosphate.

Hydrogen is most readily determined by explosion when it is not associated with more than one hydrocarbon of the methane series, but it is often necessary to remove hydrogen from a mixture of paraffins prior to the explosion and after the absorption of CO_2, CO, olefines, etc. Paal and Hartmann[1] introduced the use of colloidal palladium. The solution is made up by dissolving 2·44 gm. Kalle's colloidal palladium (61·33 per cent. Pd) and 2·74 gm. sodium picrate in 130 c.c. water and is used in a Hempel pipette. The cost of this reagent prohibits its use in ordinary technical work, particularly as the absorption of hydrogen by the reagent is slow after prolonged use. It is found that methane is slightly soluble in the solution and, therefore, before use the solution must be saturated with a gas of approximately the same composition as the sample of gas remaining after absorption of hydrogen.

When the solution has absorbed a maximum quantity of hydrogen the palladium, together with the protective colloid with which it is associated, may be precipitated by means of a slight excess of dilute sulphuric acid. After filtering and washing it may be redissolved in a minimum of dilute caustic soda solution, about 2·5 c.c. N. NaOH solution per gm. of dry precipitate, to which fresh sodium picrate is added. An alternative method is to separate the palladium by dialysis.

For other methods of determining hydrogen in the presence of hydrocarbons see p. 542.

Nitric Oxide may be determined by absorption by converting it to nitrogen peroxide with an excess of oxygen, the peroxide being absorbed by caustic potash and the excess oxygen by alkaline pyrogallate (see below). Mixtures of nitrogen oxides are determined by titration (see p. 576).

Oxygen is absorbed by alkaline pyrogallate solutions. Potassium pyrogallate solution is made up by dissolving 15 gm. of pyrogallic acid in 100 c.c. water and adding this to 400 c.c. of a 33 per cent. solution of caustic potash immediately before use. This solution absorbs oxygen fairly rapidly, but after prolonged use, or while treating gases rich in oxygen, traces of carbon monoxide may be evolved. The trouble may be minimized by using a larger excess of potash and the error is entirely eliminated if a subsequent absorption of the carbon monoxide is possible. Clowes[2] found that for the analysis of oxygen prepared by Brin's process the most suitable absorbent was a solution of 160 gm. KOH and 10 gm. pyrogallic acid made up to 200 c.c.; it is claimed that no carbon monoxide is evolved when using this solution. For technical work it is often preferable to use caustic soda rather than potash on the grounds of economy. Orsat's reagent is a mixture of a concentrated solution of

---

[1] *Ber.*, 1910, **43**, 243.

[2] *B. A. Report*, 1896, 747.

25 gm. pyrogallic acid and 150 c.c. 25 per cent. caustic soda solution. Jones and Meighan[1] have thoroughly investigated the efficiency of sodium pyrogallate solutions and find that the rate of oxygen absorption increases with the dilution of the soda and is proportional to the concentration of the pyrogallic acid for any given concentration of soda. All sodium pyrogallate solutions give off carbon monoxide when used in analysing gas samples containing more than 95 per cent. oxygen. In making up solutions for air analysis the caustic soda solution should have a density not less than 1·30. A solution which, while having a fairly high rate of absorption, gives off a minimum amount of carbon monoxide is made as follows: The stock soda solution is made by dissolving caustic soda sticks in an equal weight of water; the stock pyro solution is made by dissolving 1 part of pyrogallic acid in 3 parts of water; when ready for use, 5 parts of the soda solution are mixed with 2 parts of pyro solution. Solid phosphorus in thin sticks is also used as an absorbent; this may be conveniently used in the absorption pipettes of many forms of apparatus (e.g. Orsat) if it is kept under water and so placed that it comes in contact with the gas when the water is displaced by gas entering the pipette. The oxidation of the phosphorus is slow unless carried out in a warm atmosphere. Sodeau uses phosphorus in a pipette immersed in a jacket containing warm water. Travers[2] suggests the absorption of oxygen by phosphorus vapour when combustible gases are absent. This method has been employed by Watson[3] and by Aston[4] for the determination of the oxygen content of air.

Franzen[5] uses a solution containing 50 gm. sodium hyposulphite in 250 c.c. water mixed with 40 c.c. caustic soda solution (500 gm. NaOH in 700 gm. H_2O) as an absorbent for oxygen in the Hempel pipette. For use in the Bunte burette he prefers a solution of 10 gm. $Na_2S_2O_4$ in 50 c.c. water to which is added 50 c.c. 10 per cent. caustic soda solution. Another absorbent used for commercially prepared oxygen consists of copper wire kept clean and moist by means of a solution composed of equal volumes of ammonia (sp. gr. 0·930) and of a saturated solution of commercial ammonium carbonate. The oxygen is absorbed by the exposed surface of moist copper, the sub-oxide formed being afterwards dissolved by the ammonia solution.[6]

Propylene and the higher olefines are absorbed by concentrated sulphuric acid (see Benzene above).

Sulphur Dioxide is readily absorbed by caustic potash, and in the absence of carbon dioxide may be thus determined. When it is desired to differentiate between CO_2 and SO_2, the SO_2 may be titrated with iodine solution (see p. 574) or it may be determined by absorption in a solution of chromic acid made by dissolving 450 gm. chromic acid in 1000 c.c. water, to which 450 gm. phosphoric acid (sp. gr. 1·70) are added and the solution brought to the boil and cooled before use.

Sulphuretted Hydrogen.—It is recommended that this gas be determined by titration (see p. 334), but if only a small sample of gas is available the sulphuretted hydrogen may be absorbed in an acid solution of copper sulphate. The solubility of carbon dioxide in this reagent is also appreciable and the same precautions must be taken as when using sulphuric acid alone for the absorption of ammonia.

---

[1] *J. Ind. Eng. Chem.*, 1919, **11**, 311-316.

[2] *The Experimental Study of Gases*, 1901, p. 83.

[3] *J. C. S.*, 1911, **99**, 1460.

[4] *Ibid.*, 1919, **115**, 472.

[5] *Ber.*, 1906, **39**, 2069.

[6] See *Thorpe's Dictionary*, 1913, vol. iv., p. 44.

The order in which the various absorbents mentioned above are used must be carefully considered. In some cases alternative absorbents have been given for the same gas or group of gases and the choice will in part depend upon whether any particular constituent of the gaseous mixture is being especially determined. It is difficult, therefore, to make a general statement of the order in which absorbents are to be used which will cover all cases. Probably coal gas is the most complex gas mixture which is ordinarily submitted to the chemist for analysis and it will serve as a guide for other operations if this is taken as an example.

Rhead and Wheeler[1] working with the Bone and Wheeler apparatus (q.v.) absorbed the constituents of the gas from the distillation of coal with the following reagents in the order named:—

Gas	Reagent
Ammonia	10 per cent. sulphuric acid.
Benzene (and higher olefines)	Concentrated sulphuric acid.
Sulphuretted hydrogen . .	Acid solution of copper sulphate.
Carbon dioxide . . .	33 per cent. solution of caustic potash.
Oxygen	Alkaline solution of potassium pyrogallate.
Acetylene	Ammoniacal solution of silver chloride.
Ethylene	Bromine-potassium bromide solution.
Carbon monoxide . . .	Ammoniacal solution of cuprous chloride.

Hydrogen was absorbed from the gas remaining after these absorptions by means of oxidized palladium (see p. 550) and methane and ethane were estimated by explosion with oxygen (see below).

To make an accurate analysis in such detail as this, requires considerable experience and manipulative skill, but the process can often be considerably shortened where results are required with moderate accuracy only. Ammonia and sulphuretted hydrogen are absent from purified coal gas. In many cases, benzene, acetylene, and all the olefines are absorbed together in bromine. Paraffins other than methane may be for technical purposes assumed absent from many industrial gases and then the somewhat difficult absorption of hydrogen may be omitted, the explosion analysis being relied upon for the hydrogen and methane figures.

INDIRECT DETERMINATION.

Many gases are determinable in an indirect manner by exploding them with another gas and noting the change in volume, or the quantity of their products of decomposition, or by a combination of these two methods. Thus for example, oxygen may be determined by exploding with excess of hydrogen, and observing the contraction; hydrogen may be determined by exploding with excess of air or oxygen, and observing the contraction; and methane by exploding with air or oxygen, observing the contraction and determining the quantity of carbon dioxide generated. In many cases valuable information is obtained if the excess of oxygen after explosion is absorbed and a calculation made of the amount of oxygen consumed during the explosion.

---

[1] *J. C. S.*, 1910, **97**, 1923.

Preparation of Pure Oxygen.—The oxygen required is conveniently prepared by heating pure potassium permanganate in a small round bottomed flask. The flask is about half filled with dry potassium permanganate and then fitted with a rubber stopper and delivery tube connecting with a washing bottle containing caustic soda solution to arrest any carbon dioxide formed by the combustion of dust, and also any manganese dioxide dust carried forward. The flask is gently heated and the gas issuing from the washing bottle is allowed to escape for some time to ensure the expulsion of atmospheric air. Connection is then made with the explosion vessel or eudiometer, or preferably with a small gas holder where the oxygen may be stored over glycerine or brine.

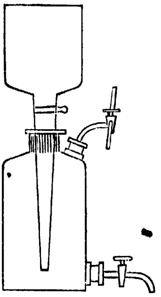

Fig. 91.

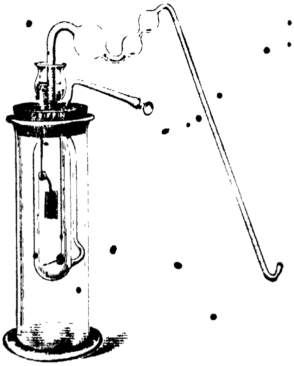

Fig. 92.

A convenient type of gas holder, the use of which involves the minimum number of rubber joints is shown in fig. 91. Both taps are attached to the holder by ground-in joints and the gas tap has three limbs (Fig. 69).

The gas should be tested for purity before use, and at least 99·5 per cent. of the volume should be absorbed by alkaline pyrogallate.

Oxygen may also be prepared by heating pure potassium chlorate in a small retort made of combustion tubing. A bulb is blown at the closed end of the tube and about half filled with dry powdered potassium chlorate. The neck of the retort is then drawn out and bent to form a delivery tube connecting with a washing bottle as described above. Oxygen prepared in this manner may contain traces of ozone.[1]

Preparation of Pure Hydrogen.—Any hydrogen required in gas analysis must be prepared by electrolysis, since that from other sources is liable to contamination with impurities which would vitiate the analysis. Bunsen's apparatus for this preparation is shown in fig. 92. It consists of a glass tube closed at the lower end and with a funnel at the other, into which a delivering tube is ground, the funnel acting as a water joint. Two platinum wires are fused into the tube, one being attached to a strip of platinum foil and the other being immersed in zinc amalgam placed in the bottom of the tube. The tube is nearly filled with dilute sulphuric acid and, as shown in the diagram, the whole apparatus is immersed in a cylinder of water for cooling purposes. On connecting the platinum wires with a battery of two or three cells, the platinum foil being made the negative electrode, pure hydrogen is evolved, which after expulsion of the air may be passed into the explosion vessel or into a holder. After some time the layer of liquid just over the zinc amalgam becomes saturated with zinc sulphate, this is then expelled through the side tube by pouring fresh acid through the funnel.

---

[1] Oxygen may also be very conveniently prepared by the interaction of a 5 per cent. acid solution of potassium permanganate and a 10 vol. solution of hydrogen peroxide.

An apparatus for preparing hydrogen and oxygen by electrolysis is shown in fig. 93. Two platinum plates, each on the end of a short platinum wire, are each covered by a glass hood fused to a delivery tube at the top as shown. Each platinum wire is fused into the closed end of a bent glass tube which is filled with mercury. The two gas delivery tubes and the two tubes containing mercury pass through the rubber cork fitted in the top of the outer cylinder. The cylinder being nearly filled with 5 per cent. sulphuric acid and the wires from a low voltage battery being dipped into the open tops of the mercury tubes, hydrogen and oxygen respectively are evolved from the negative and positive electrodes and may be separately collected. In order to avoid the formation of ozone the current used should not exceed 0·1 ampere per sq. cm. of electrode surface. Traces of hydrogen may be removed from the oxygen by passing over heated copper oxide and traces of oxygen removed from the hydrogen by passing over heated metallic copper.

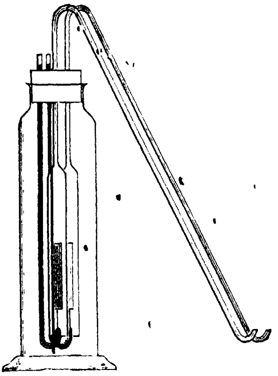

FIG. 93.

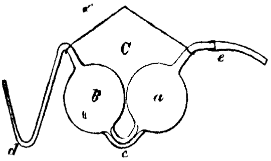

FIG. 94.

If gas holders are not available for storing these gases they may be stored in thick-walled test tubes over mercury, and a useful apparatus for transferring the gas to the analysis apparatus is shown in fig. 94; *a*, *b*, are glass bulbs of about 50 mm. diameter, connected by a glass tube, the bore of which is constricted at *c*, so as to allow mercury to pass but slowly from one bulb to the other and thus control the passage of gas through the narrow delivery tube *d*. The other end *e* is provided with a short piece of rubber tubing, by blowing through which any desired quantity of gas may be readily delivered. Care must be taken after use that the delivery tube is not removed from the trough till the angle *d* is filled with mercury. To replenish the pipette with gas, fill the bulb *b* and the tubes *c* and *d* with mercury; introduce the point of *d* into a tube of gas standing in the mercury trough, and draw air from the tube *e*. The gas in *b* is confined between the mercury in *c* and that in *d*.

Explosive Mixtures.—The degree of accuracy attainable at this stage of the analysis depends mainly upon having a suitable mixture of gas before explosion. In order to moderate the violence of the explosion and in order to prevent the formation of oxides of nitrogen, care must be taken that the concentration of the combustible gas is not too high. If necessary, the mixture is diluted with air, but it is usually more convenient simply to add an excess of oxygen. Any dilution which would prevent the explosion from taking place or, what is worse, cause incomplete combustion on explosion must, however, be avoided. The spark is most conveniently derived from an induction coil capable of giving a half-inch spark and should not be continued longer than is necessary, or an appreciable quantity of nitrogen (if present) may be oxidised.

The determination of the quantity of oxygen which must be added to combustible gases so as to prevent the explosion from being too violent, and at the same time to ensure complete combustion, has been the subject of much experiment. When the gases before explosion are under a pressure equal to about half that of the atmosphere, the following proportions of the gases must be employed:—

	Volume of Combustible Gas.	Volume of Oxygen.
Hydrogen	1	1·5
Carbonic oxide	1	1·5
Methane	1	5
Gases containing two atoms of carbon in the molecule, as Ethane C_2H_6	1	10
Gases containing three atoms of carbon in the molecule, as Propane, C_3H_8	1	18
Gases containing four atoms of carbon in the molecule, as Butane, C_4H_{10}	1	25

In cases of mixtures of two or more combustible gases proportionate quantities of oxygen must be introduced.

Thomas[1] worked with a much smaller excess of oxygen and carried out the explosion at a lower pressure. Thus, when determining by explosion the amount of oxygen in a sample of air he added half a volume of hydrogen to the air and exploded at a pressure of 400 mm. When exploding combustible gases the amount of oxygen to be added and the pressure to which the mixture is to be reduced before explosion are shown in the following table:—

---

[1] *J. C. S.*, 1879, **35**, 213.

Name of Gas.	Volume of Combustible Gas.	Volume of Oxygen to be added.	Pressure of Mixture before exploding.
Hydrogen	1	1	200 mm.
Carbon monoxide	1	1	200 mm.
Methane	1	2·5	170 mm.
Acetylene	1	3	150 mm.
Ethylene	1	3·5	145 mm.
Ethane	1	4	140 mm.
Propylene	1	5	135 mm.
Propane	1	5·5	130 mm.
Butylene	1	6	125 mm.
Butane	1	7	120 mm.

Obviously, if a large quantity of incombustible gas is present in the sample of gas about to be exploded it will be necessary to enrich the mixture with some explosive mixture. Electrolytic gas ($2H_2 + O_2$) is the only such mixture whose addition would not interfere with the subsequent calculation of results. The addition of electrolytic gas to mixtures weak in combustible gas is rendered unnecessary in apparatus fitted with a platinum spiral which can be kept incandescent for a sufficient time to achieve complete combustion.

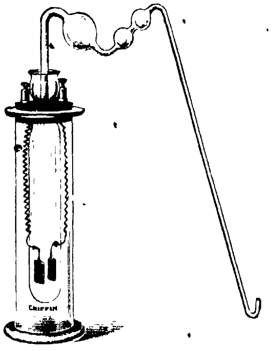

FIG. 95.

The Preparation of Electrolytic Gas.—Bunsen's apparatus for this preparation is shown in fig. 95. The tube with funnel into which is ground a delivery tube, and the outer water jacket are the same as in the apparatus described for the preparation of pure hydrogen (fig. 92). The two platinum wires fused into the side of the tube are each connected to a strip of platinum foil. The tube is nearly filled with 5 per cent. sulphuric acid and the platinum wires connected to a battery. The current density employed must be low—of the order 0·1 ampere per sq. cm.—or ozone which gives an incorrect gas mixture and attacks the mercury in the explosion vessel will be formed. This mixture should be either stored over mercury or passed direct into the explosion vessel. Storage over water would result in solution of one of the constituents, after which the mixture itself would leave some residual gas after explosion.

Calculation of Results of Explosion Analysis.—As previously explained, three experimental results are obtainable from the explosion analysis:—

(1) The change in volume, which we will denote by C.

(2) The volume of CO_2 formed and subsequently absorbed in potash, which we will denote by A.

(3) The oxygen consumed during the explosion, which we will denote by Ox.

If it is known that only one explosive constituent was originally present in the gas the volume of it is readily calculated from one of the above results by reference to the data given in Table B. For example, if hydrogen alone were present the contraction in volume after explosion would be divided by 1·5 to give the volume of hydrogen in the sample.

A very common mixture to be determined by explosion is one of hydrogen and methane. Suppose x vols. H_2 and y vols. CH_4 originally present in the sample; x and y are given by the equations

$$C = 1\cdot5x + 2y$$
$$A = y$$

If z vols. of CO were also present in the mixture it would be necessary to determine Ox and then solve the three equations

$$C = 1\cdot5x + 2y + 0.5z$$
$$A = y + z$$
$$Ox = 0\cdot5x + 2y + 0\cdot5z.$$

TABLE B.*

THE VOLUME OF OXYGEN CONSUMED, THE VOLUME OF CO_2 PRODUCED, AND THE CONTRACTION OF VOLUME CONSEQUENT UPON THE COMPLETE COMBUSTION OF UNIT VOLUME OF VARIOUS GASES.

Gas.	Molecular Formula.	Volume of Oxygen Consumed (Ox)	Contraction of Volume Consequent on Complete Combustion (C).	Volume of CO_2 Produced on Complete Combustion (A)
Acetylene	C_2H_2	2·5	1·5	2
Benzene	C_6H_6	7·5	2·5	6
Butane	C_4H_{10}	6·5	3·5	4
Butylene	C_4H_8	6	3	4
Carbon monoxide	CO	0·5	0·5	1
Cyanogen	$(CN)_2$	2	0	2
Ethane	C_2H_6	3·5	2·5	2
Ethylene	C_2H_4	3	2	2
Hydrogen	H_2	0·5	1·5	0
Methane	CH_4	2	2	1
Pentane	C_5H_{12}	8	4	5
Propane	C_3H_8	5	3	3
Propylene	C_3H_6	4·5	2·5	3

* For the sake of simplicity it is assumed in this Table that the molecular volumes of all gases are the same. Burrell and Seibert[1] have pointed out

---

[1] *U.S. Bureau of Mines*, Tech. Paper No. 54.

Oxygen, nitrous oxide and nitric oxide require separate consideration as combustion in these cases is effected with hydrogen. The corresponding factors are given herewith.

Gas.	Molecular Formula.	Volume of Hydrogen Consumed per Unit Volume (H).	Contraction of Volume Consequent on Complete Combustion of Unit Volume with H_2 (C)	Volume of CO_2 Formed.
Nitric oxide . .	NO	1	1·5	0
Nitrous oxide . .	N_2O	1	1	0
Oxygen . . .	O_2	2	3	0

The analysis of gases containing more than one hydrocarbon of the series C_nH_{2n+2} presents some difficulty. In the first place, hydrogen and all gases other than paraffins and nitrogen must be previously removed by some other method. Then, if it is known or can be assumed that only two paraffins are present, calculation may be made as in the following example:—

Gas contains x vols. CH_4 and y vols. C_2H_6.

$$C = 2x + 2{\cdot}5y$$

$$A = x + 2y.$$

When more than two paraffins are present the respective quantities cannot be determined. In this connection it is important to bear in mind that a mixture of one volume of methane with one volume of butane would give the same results on explosion as two volumes of propane. The nature of the mixture can only be estimated from a consideration of the ratios between the observed values for C, A, and Ox. The ratios $\frac{C}{A}$ and $\frac{C}{Ox}$ for the paraffins are as follows:—

	$\frac{C}{A}$	$\frac{C}{Ox}$
Methane . . .	2·000	1·000
Ethane . . .	1·250	0·711
Propane . .	1·000	0·600
Butane . . .	0·875	0.531
Pentane . . .	0·800	0·500

---

that this assumption involves an appreciable error when calculating the results of an explosion analysis. For example, it would be more accurate to state the volume relationships as follows (cf. figures for relative density Table A, p. 599):—

(1) 1·002 vol. H_2 consumes 0·500 vol. O_2.

(2) 0·999 vol. CH_4 consumes 2·000 vols. O_2 producing 0·994 vol. CO_2.

(3) 0·990 vol. C_2H_6 consumes 3·500 vols. O_2 producing 1·988 vol. CO_2.

Even when these more accurate figures are taken there is still an error (the magnitude of which is seldom calculated) due to the assumption that the molecular volume of a given gas under standard conditions is the same whatever the partial pressure from which it is deduced. Haber[1] recommends that the partial pressure of the CO_2 produced by the combustion should not exceed 35 per cent. of the total pressure.

[1] *Thermodynamics of Technical Gas Reactions*. 1908. p. 308.

Burgess and Wheeler[1] determined the nature of the paraffins obtained from the distillation of coal by calculating the number of CH_2 groups present in unit volume of the mixed paraffins as follows.

Any volume V of a mixture of paraffins is supposed to contain mCH_4 groups and nCH_2 groups

Obviously we may write $V = m$.

Furthermore, the reaction on explosion may be expressed by the equation

$$(mCH_4 . nCH_2) + (2m + 1{\cdot}5n)O_2 = (m + n)CO_2 + (2m + n)H_2O.$$

Therefore

$$C = m + (2m + 1{\cdot}5n) - (m + n) = 2m + 0{\cdot}5n$$

and $$A = m + n.$$

On solving these equations we find

$$m = \frac{2C - A}{3},$$

and $$n = \frac{2(2A - C)}{3}$$

whence $$\frac{n}{V} = \frac{n}{m} = \frac{4A - 2C}{2C - A}.$$

The nature of the olefines in coal gas may be approximately estimated by exploding a separate sample, determining the total carbon dioxide formed and subtracting the carbon dioxide due to other constituents.

Calculation of Nitrogen Content from Explosion Analysis — It is a common practice when writing down the results of a gas analysis to estimate the nitrogen by difference. The nitrogen figure then bears the accumulated experimental errors of the whole analysis; it is recommended that it should be determined directly if a second sample of the gas is available (see p. 544).

In many cases nitrogen may be determined from the results of the explosion analysis by simply noting the volume of residual gas after the absorption of excess oxygen, but the figure may then be erroneous due to impurities in the oxygen or to incomplete combustion on explosion.

An alternative method of determining the excess of oxygen after explosion is to mix the residual gas, after absorption of CO_2, with an excess of hydrogen and submit it to a second explosion; the oxygen content is then one-third of the contraction in volume.

FRACTIONAL COMBUSTION.

The practice of fractional combustion in gas analysis is dependent upon the ascertained phenomenon of the different ease of oxidation of the gases methane, carbon monoxide, and hydrogen. A variety of oxidizing agents has been introduced from time to time, but cupric oxide is the one which has hitherto given the most consistent results and is the one most generally employed. In addition to fractional combustion typified by the case of the use of cupric oxide, a number of what may be termed slow combustion methods have been introduced. These methods depend upon the oxidation of the constituents of a carbon monoxide, methane,

[1] *J. C. S.*, 1914, **105**, 133.

and hydrogen mixture by passage of the gaseous mixture, together with sufficient oxygen or air for oxidation, over heated palladium or platinum. By *careful* regulation of the temperature of the metal, preferential combustion of some of the constituents of the mixture can be secured. We propose to discuss briefly the various methods employed, but it must be pointed out that the accuracy and reliability of some of the methods of *preferential* combustion still require further investigation.

Fractional Combustion Employing Cupric Oxide.—In the practice of this method, the gaseous mixture of CO, H_2, and CH_4 is passed backwards and forwards a number of times over a mass of cupric oxide heated first of all to a temperature of about 250° C. and finally to bright redness. In these circumstances it is claimed that (*a*) at about 250° C. hydrogen and carbon monoxide are completely oxidized while (*b*) at a bright red heat the methane is completely oxidized. This being the case, subsequent measurement of the contraction in volume and measurement of the volume of carbon dioxide produced at each stage would enable a complete analysis of the CO, H_2, CH_4 mixture to be made. It is seen, therefore, that the accuracy of the method is entirely dependent upon the truth or otherwise of the assumption of complete oxidation of the various constituents. The matter has been examined in detail by Terres and Maugnin[1]. Their apparatus consisted of a tube of Jena glass bent into a spiral, having an internal diameter of 10 mm. and a length of 800 mm. packed with copper oxide. The spiral was raised to the desired temperature by immersion in a bath of potassium and sodium nitrates. Their conclusions are as follows:—

(1) *Carbonic Oxide.*—Dry carbonic oxide when not mixed with other combustible gases is never completely burned at the usual temperature of fractional combustion. Even in the volumetric analysis of a mixture containing a large proportion of carbonic oxide, quite erroneous results may be obtained at the customary temperature. At a red heat, however, the combustion of carbonic oxide is complete. Alone and in the dry state, 90 to 94 per cent. of the gas is burnt at 305° C.

(2) *Hydrogen.*—The combustion of hydrogen commences at 160° C. to 170° C. and is complete at 250° C.

(3) *Carbonic Oxide and Hydrogen.*—The presence of hydrogen is known to lower the temperature of combustion of carbonic oxide and other gases, and owing to this fact carbonic oxide in the presence of small quantities of hydrogen is completely burned at lower temperatures than that required in the absence of hydrogen. It seems possible to secure complete quantitative fractional combustion of a carbonic oxide—hydrogen mixture and separation from methane by combustion with cupric oxide at 300° C., provided the mixture is composed of approximately equal proportions of carbonic oxide and hydrogen on the one hand and methane on the other.

(4) *Methane.*—The combustion of methane over cupric oxide begins at 310° C. When methane is present in very small proportion the combustion is not quite complete even at a red heat. In high concentration the combustion of methane is complete at a red heat.

---

[1] *Journal für Gasbeleuchtung*, 1915. See also J. *Gas Lighting*, 1915, **129**, 257.

(5) *Heavy Hydrocarbons* such as acetylene, ethylene, and benzene do not burn quantitatively at 300° C., even in the presence of hydrogen, owing to deposition of carbon.

Jaeger's Method.—In the actual practice of fractional combustion with cupric oxide as introduced by Jaeger[1], fractional combustion of hydrogen and methane alone is carried out, CO being determined by previous absorption; the copper oxide is contained in a small tube of hard Jena glass of the form shown in fig. 96. The tube ends in a capillary on one side and in a somewhat wider tube on the other. The cupric oxide is introduced through the wider end, a little large-grained cupric oxide being first of all introduced (retained in place near the capillary end of the tube by a plug of asbestos fibre), the remainder of the tube being then filled with ignited finely-powdered cupric oxide, the whole being retained in position by a second asbestos plug. When in use, the tube is connected on the one side with the measuring burette and on the other with the absorption pipette containing potassium hydroxide solution for CO_2 absorption. The tube can be heated by a Bunsen burner provided with a special regulating tap, and the head is adapted so that a fan-shaped flame is obtained whereby the whole of the oxide is heated. Attached to the burner is a framework of sheet iron. This carries a thermometer which lies close to the side of the combustion tube. The absorbing liquid in the absorption pipette is first of all adjusted to the fixed mark P, which is taken as the zero for measurements of volume. The combustion tube is now slowly heated to 250° C. and this temperature maintained with the minimum variation possible. The gas is now slowly passed from the burette over the heated oxide a number of times, until, on adjusting the potash level again to P, the measured volume remains constant, the gas having been allowed to cool before the measurement of volume is made. The correction of volume necessitated by the oxygen contained initially in the combustion tube is ascertained once for all by filling the burette with pure hydrogen and carrying out the combustion of this gas by means of the cupric oxide. A part of the oxygen necessary for the oxidation of the hydrogen is obtained from the air initially filling the combustion tube, and the contraction in volume on oxidation is consequently greater than it would be if the whole of the necessary oxygen were derived from the cupric oxide. The correction is ascertained by deducting the theoretical diminution of volume from the ascertained value. The difference is the

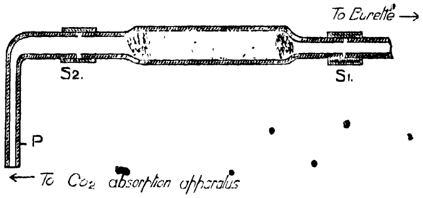

FIG. 96.

---

[1] *J. Gasbeleucht*, 1898, 41, 764.

correction and is to be subtracted from any subsequent reading of contraction. The correction must likewise be applied when the nitrogen content of the sample of gas analyzed is determined. The hydrogen having been preferentially oxidized at 250° C. or so, the cover and thermometer are removed and the combustion tube raised to a bright red heat, and the gas is passed to and fro over the heated cupric oxide until, after absorption of the CO_2 produced, the final volume of the gas remains constant. The volume of CH_4 originally present corresponds with the volume of CO_2 produced and absorbed by the potash, so that the contraction in volume corresponds exactly (without the above correction) to the volume of methane present. The nitrogen content of the sample is obtained by adding to the volume of the residual incombustible gas the correction value for consumed oxygen derived from the air in the tube, ascertained as above.

Taplay[1] uses the cupric oxide in the form of a rod supported on silica loops so as to lie along the axis of a fused silica combustion tube. According to Wibaut,[2] the reaction between cupric oxide and hydrogen or methane is slow and the end point is ascertainable only with difficulty, consequent upon the slight diminution of volume accompanying oxidation being masked by the increase of volume of the gas, due to increase of temperature by passage of the gas over the heated cupric oxide. Wibaut finds the velocity of the reaction considerably accelerated by the use of a mixture of cupric oxide and cerium dioxide, in relative proportions such that the resulting mixture is greyish-white in colour.

The Direct Determination of Nitrogen.—As already mentioned, it is a very customary practice to ascertain the nitrogen content of a gaseous mixture by difference, but this cannot be regarded as completely satisfactory. When the nitrogen can be directly determined, a check is obtained upon the accuracy of the rest of the analysis, and furthermore a knowledge of the nitrogen content of industrial gases is of growing importance and demands direct determination. The principle of the method employed is based upon the well-known Dumas' method of determining the nitrogen in organic compounds. Jaeger (loc. cit.) using the apparatus already described, determined the nitrogen content alone of a gas sample by heating the cupric oxide directly to a bright red heat and passing the gas sample a number of times over the heated oxide until the final volume after cooling remained constant. The whole of the gaseous components of the mixture except nitrogen were in this manner removed. The residual volume after cooling was then determined, and the correction for the oxygen of the air being partly responsible for the oxidation process (ascertained as before) was added. When the air in the copper oxide tube was replaced by nitrogen previous to the test, no correction of this kind was necessary. The reduced copper was re-oxidized to cupric oxide after each test by heating in a current of air.

Smith[3] described a method, based upon similar principles, for dealing with larger volumes of gas.

---

[1] *J. Gas Lighting*, 1918, **144**, 870.

[2] *Chem. Weekblad*, 1914 ; *J. Gas Lighting*, 1914, **127**, 174.

[3] *J. S. C. I.*, 1899, **18**, 213.

Evans[1] has devised the "Metrogas" apparatus for this determination. The sample of gas under examination is subjected to the action of heated copper oxide, whereby all the combustible constituents and the oxygen in the gas are converted to carbon dioxide and water vapour; subsequent absorption with a solution of caustic soda leaves only the nitrogen originally present in the gas, and this is measured directly. The correction due to absorption of oxygen is eliminated by using externally generated carbon dioxide.

The apparatus, fig. 97, consists essentially of a graduated alkali burette A, containing caustic soda solution, an acid burette B, containing acidulated water, a quartz tube C, containing copper oxide, a sampling burette D, containing acidulated water, and a carbon dioxide generating apparatus E.

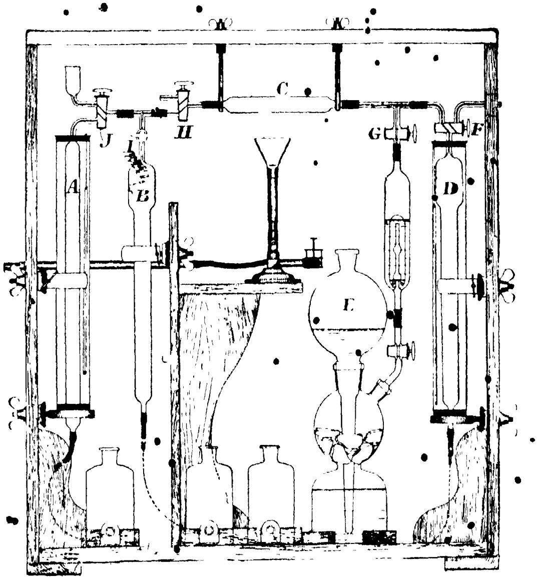

FIG. 97.

The apparatus having been proved gas-tight, all air is expelled from the quartz tube and capillary connection by means of carbon dioxide. The sample of gas is drawn into the burette D and measured off at a known temperature; it is then passed slowly through the tube C, heated to redness, into the burette B. The gas is passed backwards and forwards between B and D several times, after which the residual gas is completely swept into B by means of carbon dioxide. The stop cock H is closed and the nitrogen-carbon dioxide mixture in B is transferred to A for absorption of carbon dioxide and measurement of nitrogen. If necessary, correction is made for the difference between the temperature of the nitrogen in A and the original temperature of the gas when measured in D.

---

[1] *Gas World*, 1911, **55**, 811 ; *J. Gas Lighting*, 1911, **116**, 819.

Balcon[1] and Smith[2] have described modifications of the Bone and Wheeler apparatus (q.v.) whereby nitrogen may be directly determined in a somewhat similar manner.

Combustion Methods Employing Palladium or Platinum.—A number of experimenters have developed the processes of fractional combustion of gaseous constituents employing palladium, or platinum as catalysts, whereby the oxidation process is very considerably accelerated. The oxidation process is carried out by bringing the combustible gases mixed with an excess of air or oxygen into intimate contact with a wire or tube of the metal in question. According to Winkler,[3] methane is not burnt at all when passed over palladium asbestos kept heated by a naked flame, and even in the presence of considerable excess of easily combustible gases, there is, if any, only a slight trace of methane burnt. Hempel[4] states that methane when passed over palladiumized asbestos does not burn at all at temperatures up to 100° C. The combustion begins at about 200° C. Above 200° C., a portion of the methane is burnt along with the hydrogen. Phillips[5] gives the temperature of oxidation of methane by palladiumized asbestos as 404°-414° C., and he further states that a variation in the proportion of inflammable gas and air does not seem to affect the oxidation temperature. Richardt[6] found that appreciable oxidation of methane in the presence of palladiumized asbestos was not obtained until a temperature of 600° C. was reached. He states that for fractional combustion of hydrogen, using palladiumized asbestos, the temperature must not exceed 500°-600° C. Denham[7] concludes that the temperature of combustion of practically pure methane and oxygen lies between 514° C. and 546° C. Further, a variation in the volumes of the gases (methane and oxygen) present exercises an influence on the necessary temperature, tending to raise it above that recorded for a gaseous mixture in proper proportion for complete combustion. The usual method of fractional combustion of hydrogen in the presence of methane, using palladiumized asbestos, gives reliable results if the temperature does not rise above 500° C.-550° C. In no case did Denham find anything approaching complete combustion of methane, although the gas was in some cases at 100° above its temperature of combustion. This is in agreement with the result of Richardt, who found only 1·3 per cent. of the methane burnt at 600° C.

Combustion Method Employing Palladium.—This method can be employed to give reliable results when used for the determination of hydrogen and carbon monoxide in the presence of methane. The palladium can be employed either in the form of wire or of palladiumized asbestos. Palladium wire is recommended by **Bunte**,[1] and is used in the form of a very thin filament about 15 mm. long. The wire is inserted in the constriction produced by drawing down a tube of potash glass. Plugs of asbestos fibre are inserted in the unrestricted portion of the tube. **Richardt** recommends the tube to be heated to a temperature such that the characteristic yellow colour of sodium is imparted to the tip of the flame employed.

---

[1] *J. Gas Lighting*, 1913, **121**, 102. [2] *Gas World*, 1919, **71**, 342.

[3] See Lunge, *Technical Gas Analysis*, 1914, p. 167.

[4] *Methods of Gas Analysis*, 1892, p. 134.

[5] *American Chemical Journal*, 1894, **16**, 163-187.

[6] *J. Gasbeleucht*, 1904, **47**, 566-570 and 590-595.

[7] *J. S. C. I.*, 1905, **24**, 1202.

Palladiumized asbestos for this purpose was introduced by **Winkler** and is prepared as follows:—

One gm. of palladium is converted into chloride by the action of HCl, and then reduced by the addition of a cold saturated solution of sodium formate, sufficient sodium carbonate being added to make the solution strongly alkaline. About 1 gm. of asbestos fibre is placed in the solution and removed after becoming saturated with the solution, and dried at a gentle heat. The asbestos is then washed with boiling water and finally well dried.

The combustion tube employed is about 1 mm. internal diameter and about 8 cm long, and is filled over a length of about 1 cm. by twisting together a few threads of the moistened palladiumized asbestos and pushing them into the tube, the asbestos being finally dried by heating over a water bath.

The tube containing either palladium wire or asbestos is inserted between the absorption pipette and the measuring burette, as already described in the case of fractional combustion with cupric oxide. The heating of the wire or asbestos is done by means of a spirit lamp or very small burner and, when asbestos is employed, the combustion having been so initiated, continues without further application of heat.

Combustion Methods Employing Platinum.—Instead of palladium, platinum may be used to accelerate the combustion of gases such as carbon monoxide, hydrogen, and methane. The platinum is used in the form of wire or in the form of a tube. Various arrangements have been devised for carrying out the process:—

(1) *The Winkler-Dennis Combustion Pipette.*[2]—This consists of an ordinary **Hempel** pipette modified by the introduction of a spiral of platinum wire which can be maintained electrically in a state of incandescence. The instrument is not a convenient one to use. The contact between the platinum spiral and the gas is not very intimate and an explosion is liable to occur unless the gaseous mixture is led slowly into the pipette.

(2) *Drehschmidt's Platinum Capillary Tube.*[3]—This is constituted of a seamless platinum tube 10 cm. long, 2 or 3 mm. external diameter and 0·7 mm. internal diameter. The tube terminates in two cooling jackets (see fig. 98) filled with water. A few fine platinum wires are packed into the capillary and, when the tube is raised to a bright red heat, a combustible mixture passed through the tube is completely burnt. The

---

[1] *J. Gasbeleucht*, 1878, **21**, 263, and *Ber.*, 1878, **11**, 1123.
[2] *Z. a. C.*, 1889, **28**, 269 ; *J. S. C. I.*, 1889, **8**, 570.
[3] *Berichte*, 1888, **21**, 3245.

apparatus is connected to the absorption pipette and the burette as already explained.

(3) *Levy's Silica-Platinum Combustion Capillary*.[1]—This is illustrated in fig. 99. AB is a tube of fused silica about 7 mm. external diameter and 1·5 mm. bore. CD is a wire composed of an alloy of platinum with 30 per cent. of iridium. This is stretched axially along the silica tube AB. The leading-in wires EC and FD are made of molybdenum, this being the only metal which can be satisfactorily fused into silica. The molybdenum wire terminates at E and F in solid lumps of lead to which copper wires are soldered. G and H are leading-in tubes of silica about 1 mm. bore which serve to pass the gas through the tube AB and over the wire CD, which is heated by a current from a 2-volt or 4-volt battery, the temperature being regulated by means of a rheostat included in the circuit. The heated wire is corrugated so as to take up the expansion on heating. This can likewise be effected by using a straight wire and employing a short spring of molybdenum. The oxidation of a gaseous mixture is accelerated if the wall of the capillary tube receives a coating of finely-divided platinum produced by spluttering of the platinum wire.[2]

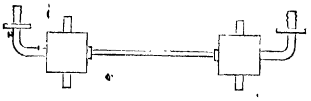

FIG. 98.

The method of combustion of a gaseous mixture using platinum gives reliable results when used for methane determinations. The limitations of the method for use in fractional combustion have not yet been specified with the same degree of precision as in the cases of cupric oxide and palladium. Levy[3] claims that by the use of the silica-platinum capillary tube an accurate analysis can be made of a gaseous mixture containing hydrogen, carbon monoxide, methane, and nitrogen. For this purpose he proposes two methods :—

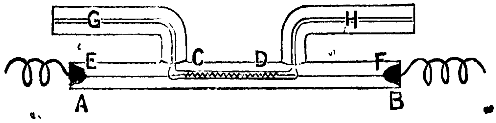

FIG. 99.

Complete Combustion Method.—In this method a few c.c. of the gaseous mixture, after removal of absorbable constituents, are measured and excess of air or oxygen added, the resultant volume being measured. The mixture is then passed a few times (2 or 3) over the platinum wire heated to incipient whiteness. After each passage the gas is allowed to cool and, when no further contraction is obtained by passage of the gas over the heated wire, the contraction is noted. The CO_2 produced is absorbed by potash, the resulting diminution of volume being noted. The excess of oxygen is absorbed by alkaline pyrogallate solution. The amount of oxygen used in the complete oxidation is thus determined, and if

---

[1] *J. S. C. I.*, 1912, **31**, 1153 ; *J. Gas Lighting*, 1913, **122**, 455.
[2] *J. S. C. I.*, 1912, **31**, 1153. [3] *J. Gas Lighting*, 1913, **122**, 457.

C = contraction on combustion
A = contraction on absorption in potash
O_c = volume of oxygen used in the oxidation

$$CO \text{ present} = \frac{4A + C - 3O_c}{3}$$

$$CH_4 \text{ present} = \frac{3O_c - C - A}{3}$$

$$H_2 \text{ present} = C - O_c.$$

Fractional Combustion Method.—Levy states that if the wire be heated to scarcely visible redness, the hydrogen and occasionally some of the carbon monoxide are burnt, while the methane is unaffected. On heating the wire to incipient whiteness, the remainder of the carbon monoxide and the whole of the methane are oxidized. Proceeding as before, at scarcely visible redness, let the contraction of volume be C_1 and the further contraction on absorption with potash be A_1. After heating to incipient whiteness let the further contraction be C_2 and the further contraction on absorption with potash A_2. Then :—

$$H_2 \text{ present} = \frac{2}{3}\left(C_1 - \frac{A_1}{2}\right) \qquad CH_4 \text{ present} = \frac{2C_2 - A_2}{3}$$

$$CO \text{ present} = \frac{A_1}{2} + \frac{4A_2}{3} - \frac{2C_2}{3}.$$

Levy recommends the complete combustion method for use in a constant volume apparatus, while for use with instruments in which measurements are made at constant pressure the fractional combustion method is to be preferred.

Amongst other methods of fractional combustion may be mentioned that introduced by Moser and Schmid,[1] in which the gaseous mixture is passed over about 20 gm. of yellow mercuric oxide contained in a U-tube, maintained at 100° C. by immersing the tube in boiling water. The resulting CO_2 is absorbed by means of standardized baryta water. The mercuric oxide is to be precipitated and dried at a low temperature and protected from the prolonged action of light. Oxide precipitated in hot solution, or the red oxide, is inactive. The oxidation of about 100 c.c. of gas requires about 45 minutes. Methane is unaffected at 100° C., while hydrogen is partially oxidized but does not influence the titration with standardized baryta water.[2]

The Absorption of Hydrogen by Metallic Palladium.—Freshly reduced metallic palladium has the property of absorbing hydrogen at ordinary temperatures, and this provides a useful method of separating hydrogen from the paraffins. Bone and Jerdan[1] have described in detail how this may be done when working with fairly large samples of gas, but their method is also applicable to the analysis of smaller samples.

---

[1] *Z. a. C.*, 1914, **53**, 217-233.

[2] A new method for the complete combustion of gas is described by Kaleta (*Chem. Zeit.*, 1922, **46**, 430), who passes the sample through a nipple into a special pipette containing a heated platinum wire in an atmosphere of oxygen. The gas is ignited and burns slowly with visible flame

Some freshly reduced palladium black, previously heated to redness in a vacuum, is placed in a small glass bulb immersed in a water bath and connected by suitably bent glass tubing to a stop-cock at each end. One stop-cock is connected to the vessel containing the gas sample and the other to a pressure gauge and Sprengel pump. The whole apparatus, except the vessel containing the gas sample, is first evacuated by means of the pump. The pump is then shut off from the palladium bulb by means of the stop-cock and the gas sample is passed into contact with the palladium. The vessel originally containing the gas is then shut off from the bulb and, the action of the pump having been stopped, the bulb is connected with the pressure gauge. The course of the absorption of hydrogen by the palladium is followed by observing the pressure indicated on the gauge; when the absorption ceases, the residual gas is drawn off by the Sprengel pump into a tube standing over mercury in the trough at the base of the pump. The water in the bath is now heated to 100° C. to expel the hydrogen previously absorbed by the palladium, this hydrogen being drawn off by the pump and discarded. Finally the bulb is evacuated at 100° C. and allowed to cool, when, if desired, the gas sample can be subjected to a second treatment. The hydrogen occluded by the palladium, however, has an appreciable vapour pressure even at ordinary temperatures, so that the last traces of hydrogen must be removed from the gas by oxidation, in contact with "oxidized" palladium.

The palladium is removed from the absorption bulb and heated to dull redness in a hard glass tube attached to a pump for the expulsion of as much occluded hydrogen as possible. It is then heated to redness in a gentle current of air until it has acquired the characteristic dark blue oxidation tint. The "oxidized" palladium is returned to the absorption bulb, which is evacuated as before. The gas sample is introduced to the bulb once more, maintained at a temperature of 100° C., and allowed to remain in contact with the oxidized palladium for 20 or 30 minutes. The residual gas may then be withdrawn through the Sprengel pump, measured and submitted to the usual explosion analysis.

Hempel absorbed hydrogen by means of oxidized palladium, and employed an apparatus similar to that shown in fig. 108 in which the connecting tube E was replaced by a U-tube immersed in a beaker of hot water and containing the oxidized palladium. The pipette C and the burette A contained water. After passing the gas several times through the U-tube, the diminution in volume represented the volume of hydrogen absorbed plus the volume of oxygen originally in the U-tube. The latter was determined once for all, so that the necessary correction could be applied to obtain the volume of hydrogen

APPARATUS USED FOR GAS ANALYSIS.

The description of even a small proportion of the various forms of apparatus designed for purposes of gas analysis would require considerably more space than can be allowed in a volume of this nature. In the following pages an attempt is made to describe the construction and use of a few typical forms of apparatus applicable to general analytical and technical work, and some of the modifications made to meet special cases.

---

[1] *J. C. S.*, 1901, 79, 1044.

Two methods of measuring gases are employed, and afford a means of dividing the forms of apparatus into two groups:—

(*a*) The volume of the gas is kept constant and measurement made of the pressure.

(*b*) The volume of the gas is measured at constant pressure.

The use of eudiometers as originally described by Bunsen involved the waste of much time while the gas attained room-temperature before measurement, and the necessary corrections for temperature and pressure were tedious.

Williamson and Russell[1] described an apparatus, by means of which the gases in the eudiometers were measured under a constant pressure, the correction for temperature being eliminated by varying the column of mercury in the tube so as to compensate for the alteration of volume observed in a tube containing a standard volume of moist air, as explained on p. 522.

This apparatus was further developed[2] by the addition of a separate laboratory vessel in which the absorptions were made.

Russell[3] modified the apparatus so that liquid reagents could be used in the eudiometer. Regnault and Reiset[4] introduced an apparatus in which the absorptions were carried out in a separate laboratory vessel and in which the pressure at which the gas was measured was observed. Frankland and Ward[5] made several important improvements in this apparatus. They introduced a third tube, made to act as a barometer, to indicate the pressure of gas in the measuring tube, thus rendering the operation entirely independent of variations of atmospheric pressure. The correction for aqueous vapour was also eliminated by introducing a drop of water into the barometer as well as into the measuring tube, so that the difference of level of mercury at once gave the pressure of dry gas. The explosion analysis was carried out in the measuring tube under reduced pressure.

McLeod[6] further improved upon these forms of apparatus by arranging a stop-cock at the bottom of the measuring tube for the admission of mercury.

Thomas[7] described an apparatus embodying the closed pressure tube of Frankland and Ward to which mercury is admitted from the bottom, as in McLeod's apparatus. This is shown in Fig. 100, and its essential feature is that the eudiometer is kept very short while the barometer tube is much longer and extends above the top of the eudiometer. The explosion analysis is carried out in the eudiometer under reduced pressure as mentioned on p. 538, and this permits the shortening of the eudiometer. By arranging for the long length of barometer tube above the eudiometer a volume of gas may be measured under nearly atmospheric pressure, and thus the accuracy of the apparatus is considerably increased. The eudiometer is 450 mm. long and has divisions 20 mm.

---

[1] *Proc. Royal Soc.*, 1857-1859, **9**, 218.

[2] *J. C. S.*, 1864, **17**, 238.

[3] *Ibid.*, 1868, **21**, 128.

[4] *Ann. Chim. Phys.* (3), **26**, 333.

[5] *J. C. S.*, 1853, **9**, 197.

[6] *Ibid.*, 1869, **22**, 313.

[7] *Ibid.*, 1879, **35**, 231.

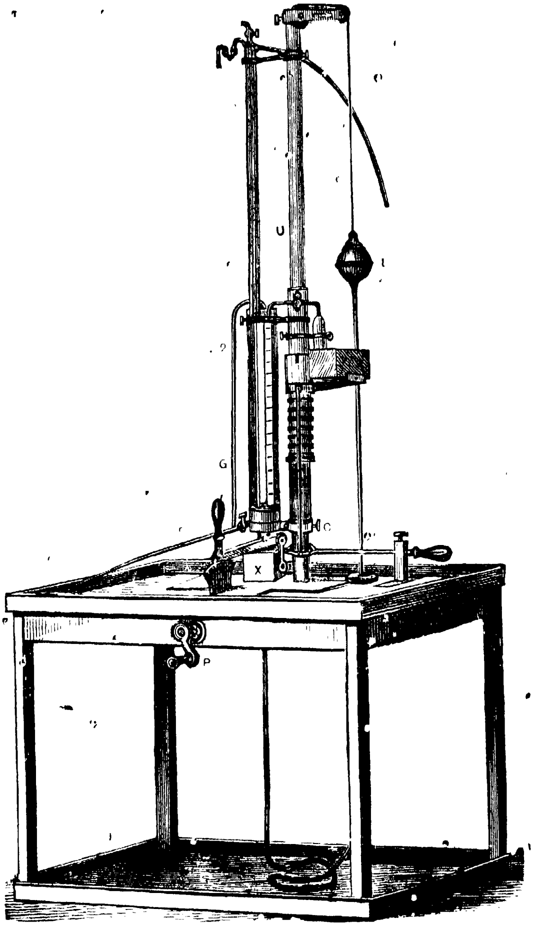

FIG. 100.

apart, the uppermost mark being placed as close beneath the platinum wires as is convenient to obtain a reading. The barometer tube is 1000 mm. in length, having about 700 mm. lines above division 2 on the eudiometer.

The steel clamp and facets forming the connections between the eudiometer and detachable laboratory tube of Frankland's apparatus are dispensed with, as in this form the eudiometer and laboratory vessels are united by a continuous capillary tube, 12 mm. (outside) diameter, and one three-way glass tap is employed in place of the two stop-cocks. The glass tap is hollow in the centre, and through this hollow a communication is made with the capillary, by means of which either the laboratory tube or the eudiometer can be washed out. As the laboratory vessel is not disconnected for the removal of the reagent used in an absorption, it is supported by a clamp, as shown in the figure; and when it requires washing out the mercury trough is turned aside for purposes of injecting a stream of water, the trough being supported on an adjustable stand to facilitate this operation. The laboratory tube is filled with mercury by sucking the air out through the capillary stop-cock. The height of the trough can be accurately adjusted and when the trough is in position, the clamp holding the laboratory vessel may be loosed if necessary.

The eudiometer and barometer tubes pass through an india-rubber stopper, as in McLeod's apparatus, but are not supported by the clamp C, which here simply supports the water-jacket. No glass stop-cocks are used, or glass work of any kind employed in the construction of the lower portion of the apparatus. The lower end of the eudiometer has a neck of the same outside diameter as the barometer tube (9·5 mm.), and both tubes are fixed into the steel block X, by the usual steam cylinder gland arrangement, small india-rubber rings being used to form the packing. The steel block is securely fixed to the table. The tap in the steel block is so devised that it first cuts off connection with the barometer tube, in order that the gas may be drawn over from the laboratory vessel into the eudiometer without risking the fracture of the upper end of the barometer tube by any sudden inrush of the mercury. By moving the handle a little further on the quadrant, a communication is made with both tubes and the reservoir, so as to take a reading; then the handle is drawn a little further to cut off the reservoir supply, whilst the way is still open between the eudiometer and barometer tubes, and if the handle be drawn forward a little more, all communication is cut off for the purpose of exploding.

The windlass P, for raising and lowering the mercury reservoir L, is placed beneath the table, in order that it may be accessible from a position opposite the laboratory vessel, and is furnished with a spring ratchet so as to be worked by one hand. The water jacket is 4 ins. in diameter, and the casing tube of the barometer as wide as practicable, so that the temperature of the apparatus may be maintained as constant as possible. To attain an accurate result it is as essential to keep the barometer tube of uniform temperature as the eudiometer, since the pressure of aqueous vapour varies considerably with temperature. The stream of water is run in through the casing tube at the upper end of the barometer, and, whilst the water-jacket is filling, the tap at the bottom is opened slightly, so that water may run out very slowly. When the water-jacket is full, the upright tube G acts as a syphon, thus keeping up the circulation at the point where it is most required. There are only two working taps in this apparatus, the three-way glass-tap between the eudiometer and the laboratory tube, and the steel tap at the base of the barometer and eudiometer. When the laboratory vessel has to be washed out after an absorption, the gas is transferred to the eudiometer until the absorbent is within a quarter of an inch of the stop-cock. As soon as the gas has passed over to the extent required, the three-way tap is turned until the through-way is at right angles to the capillary, and the way to the hollow of the tap is in communication with the laboratory vessel, then the stopper from the hollow is withdrawn so that the mercury flows out, and the laboratory vessel allowed to empty whilst the volume of the gas is read. The laboratory vessel can be washed out by means of a syringe and refilled in a very little time, as it is already connected, and, for all ordinary absorptions it is sufficient to wash the vessel out once. The explosion analysis is carried out under reduced pressure with a small excess of oxygen. When dealing with mixtures of combustible gases a suitable pressure must be chosen after consideration of the probable approximate analysis. It is better to explode at a slightly less pressure than to exceed that recommended.

Meyer and Seubert[1] have designed a gas analysis apparatus similar in many respects to that of McLeod and Thomas, but of a simpler construction and especially adapted for explosions under diminished pressure.

The Bone and Wheeler Apparatus.—The essential features of the foregoing types of apparatus were embodied in the apparatus described by Bone,[2] and Bone and Wheeler[3] have described a modification of this apparatus which can be usefully employed in most cases where accurate analyses are required. As this apparatus can be, and has been, further modified to meet special cases, it will be described in some detail.

The general character and arrangement of the various parts of the apparatus are shown in fig. 101. Its essential features are (1) a separate laboratory vessel F, standing over mercury in a trough G; (2) a measuring-tube A and a pressure tube B, both contained in a water-jacket, and to which mercury is admitted from the bottom through the tap C as in McLeod's apparatus; (3) an explosion vessel E, into which platinum wires are fused at the top, and the bottom of which is connected with a separate mercury reservoir H. The connecting tubes between A, E and F, are of capillary tubing throughout, and, as is shown, the gas in passing from one vessel to the other only comes in contact with one rubber joint. The laboratory vessel is made detachable from the rest of the apparatus for cleaning purposes. Between the vessels A and E is fused a three-way stop-cock so that, if desired, connection may be made with any suitable vessel containing the gas sample. If more convenient, the sample of gas may be introduced into the laboratory vessel through suitably bent glass tubing or from an ordinary test tube. At the top of the laboratory vessel is a three-way stop-cock, one limb of which is connected to a Winchester-quart bottle in which a partial vacuum is maintained; an ordinary water pump may be conveniently employed for this purpose and need only be

[1] *Z. a. C.*, 1885, **24**, 414.

[2] *Proc. Chem. Soc.*, 1898, p. 154.

[3] *J. S. C. I.*, 1908, **27**, 10.

used at intervals if a tap is placed between the pump and the bottle. The various parts of the apparatus are mounted on a wooden stand with vertical steel rods supporting the shelves as shown. The mercury reservoir D

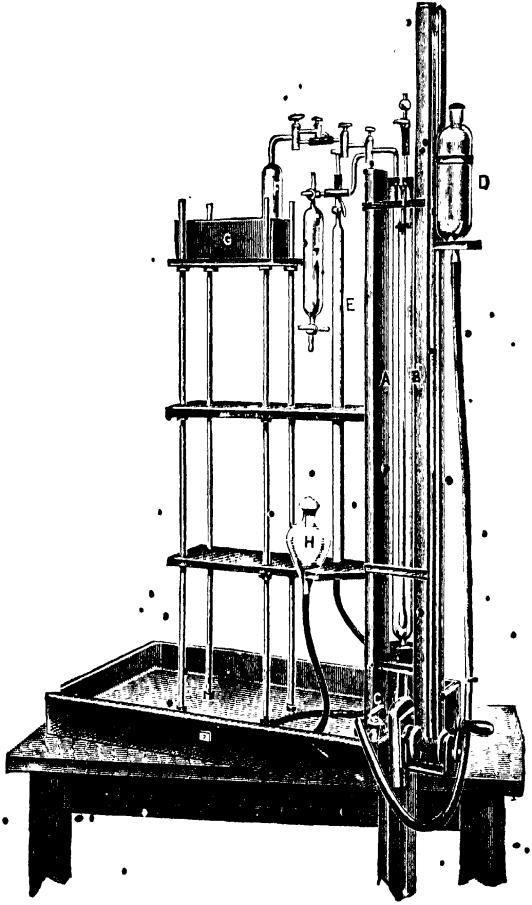

FIG. 101.

which is connected to the tap C with strong rubber tubing is supported in a wooden carrier which may be raised or lowered (to the ground level if required) by a pulley and ratchet wheel. As the tap C is subjected to considerable pressure of mercury, it is desirable to have the plug extended and drilled transversely below the barrel so as to take a wooden pin to prevent upward movement of the plug. Before commencing an analysis, care is taken that the whole apparatus is clean (it is finally washed out with a little 5 per cent. sulphuric acid), and it is proved gas tight. The whole of the apparatus is filled with mercury by raising the two mercury reservoirs and expelling all air and excess acid through the limb provided for the sampling vessel or into the laboratory vessel F. Connection is then made with the suction vessel in order to remove air and acid from F. The drop of mercury drawn over by the suction each time this operation is performed is subsequently recovered, purified, and returned to the apparatus. The principle of measurement employed is that introduced by Regnault and Reiset (loc. cit.) viz. the measurement of the pressure of the gas at constant volume. A number of constant volume marks are provided on the tube A, and when measuring the gas the mercury level in A is brought to a predetermined point by raising or lowering the reservoir D. The pressure of the gas is then determined by noting the mercury level in the pressure tube B. The mercury levels in A and B should be observed through a small telescope mounted on a vertical steel rod close to the outside of the waterjacket; opposite this telescope (at the back of the water-jacket) there should be a small electric lamp behind a ground glass screen also mounted on a vertical rod so that it can be raised or lowered to the approximate level of the mercury.

The tubes A and B are made in one piece and are surrounded by the water jacket through which water continually flows. The inner surfaces of the whole apparatus are kept just moist with 5 per cent. sulphuric acid solution. This serves as a precaution against any slight accidental fouling of the measuring tube with alkaline reagents, and, since the pressure tube B is similarly moistened, the influence of water vapour upon the gas measurements is eliminated; in fact, the various pressures noted represent those of the dry gas under examination.

At the top of the pressure tube B is a tap which allows of a vacuum being made in B whenever necessary. This tap may be connected to B by means of stout rubber tubing in order to allow a little elasticity whenever the mercury is inadvertently allowed to rise too quickly.

Since the gas is measured at a considerably reduced pressure, only a small volume of the sample (say 5 or 10 c.c.) is taken for analysis, and by selecting a suitable mark on A this may be made to have a pressure of about 100 mm. As already explained there are no corrections for atmospheric or aqueous pressures, but correction must be made for any variation of temperature during the analysis. For this purpose a thermometer is suspended inside the water jacket.

In a detailed analysis the stopcock at the top of B is repeatedly subjected to a vacuum; if it is properly lubricated there should be no leakage of air into B, but the error due to any such slight leakage or to the presence of occluded gases inside the tube may be corrected as follows. Before measuring the sample of gas the zero reading is taken by lowering D after closing the stopcocks at the top of A and B. If all is in order the level of mercury in B should be just on the zero line when that in A is brought to the lowest constant volume mark. This zero reading is taken at suitable intervals during the analysis (while the gas sample is in E or F), and any leakage into B or evolution of occluded gases will be denoted by the mercury level in B falling below zero. For the purpose of measurement it is convenient that B should be graduated for a few mm. below the zero mark. The pressure thus observed should be added to all subsequent measurements of gas pressure until the vacuum in B can be restored. The whole apparatus having been filled with mercury and the gas sample measured in A by noting the pressure in B, an absorption is carried out as follows. A few c.c. of fresh reagent are taken in a small pipette the delivery end of which is bent in a small semi-circle so that the reagent can be easily blown into the laboratory vessel when the pipette is dipped into the mercury trough. Any bubble of air introduced into F during this operation is removed by cautiously opening the tap connecting with the suction vessel. The gas sample is then transferred to F by raising D and opening the necessary taps. If a little mercury is allowed to follow the gas into F, all gas is expelled from the connecting tubes. The taps being closed, F is gently shaken until the absorption is considered to be complete. Any minute gas bubbles on the surface of the mercury under the reagent are removed by tapping F, and then the gas sample is returned to A by opening the necessary taps and cautiously lowering D until the reagent in F just rises to the tap. No appreciable quantity of any reagent must be allowed to pass the tap on F except through the limb connecting with the suction vessel. The whole of the reagent is removed through the latter limb, and after washing F with 5 per cent. sulphuric acid a little clean mercury is allowed to follow the gas into A. (The surface of the mercury in the trough is kept clean and dry by means of a little blotting paper.) The taps are closed and the gas remeasured—the diminution in pressure, after correction if necessary for temperature and zero, gives the volume of gas absorbed.

An important feature of this apparatus is that fresh reagent is taken for each absorption, thus ensuring efficiency and rapidity of absorption. The great advantage of using a small volume of reagent when a high degree of accuracy is desired arises from the smaller error due to solubility of other gases. When a small sample of gas is shaken with a relatively large volume of reagent an appreciable error may be introduced by the slight solution of gases other than the gas which it is desired to absorb; furthermore, if the reagent has been previously exposed to the atmosphere or to another gas sample it will contain some of these gases in solution and may give them up to the sample. This of course depends upon the partial pressure of the various constituents, but the error is reduced in most cases to negligible proportions when a little fresh reagent is taken for each absorption.

The following example of the method of recording the results of an analysis will illustrate the application of the corrections and the calculation of results. The sample was known to be a mixture of hydrogen, methane and nitrogen possibly containing small quantities of oxygen and oxides of carbon.

All the readings were corrected to the original temperature of 15° C. and it was found necessary to add a zero correction of 0·1 to the last three readings.

	Reading.	Temperature.	Zero.	Corrected Reading.
Gas sample . . .	131·0	15·0	0·0	131·0
After absorption by potassium pyrogallate . .	130·9	15·0	0·0	130·9 ($CO_2 + O_2 = 0\cdot1$)
After absorption by cuprous chloride . .	130·5	15·2	0·0	130·4 ($CO = 0\cdot5$ or 0·4 per cent.)
After addition of oxygen .	513·0	15·3	0·1	512·6
After explosion . .	294·0	15·3	0·1	293·8 (Contraction = 218·8)
After absorption by caustic potash	228·9	15·4	0·1	228·7 (Absorption = 65·1)

$$CH_4 = A = 65\cdot1 \text{ or } 49\cdot7 \text{ per cent.}$$
$$H_2 = \tfrac{2}{3}(218\cdot8 - 2 \times 65\cdot1) = 59\cdot1 \text{ or } 45\cdot1 \text{ per cent.}$$

Summary.

Oxygen Carbon dioxide	0·1 per cent.
Carbon monoxide	0·4 ,,
Hydrogen	45·1 ,,
Methane	49·7 ,,
Nitrogen (by difference)	4·7 ,,

Forms of Apparatus in which Measurements are made at Constant Pressure.—Dittmar[1] designed an apparatus with a water-jacketed burette, detached absorption pipettes, and a separate explosion vessel.

Macfarlane and Caldwell[2] introduced an apparatus much on the same principle but with pipettes which could be connected with the burette.

Sodeau[3] introduced an improved form of Macfarlane and Caldwell's apparatus which is shown in fig. 102. This apparatus embodies the "Kew principle" correcting tube which is explained in detail on p. 523. This correcting tube C together with the measuring tube M and the levelling tube L are fitted into a glass water jacket, which is held in position by means of a cork at A and a band clip at B. The measuring tube M is of 50 c.c. capacity graduated in $^1/_{10}$ c.c. Its upper end terminates in a capillary connected to one limb of a three-way stop-cock N placed horizontally; the other limb of this stop-cock communicates with the bent tube U partly filled with water, and by turning the tap either of these limbs may be put in communication with the capillary K, to which absorption vessels may be connected by means of rubber tubing at G. When examining samples which leave a large residue after absorption, it is convenient to replace the tube M by one having a bulb at its upper end.

---

[1] *Quantitative Chemical Analysis*, 1887, pp. 201, *et seq.*

[2] *J. West of Scotland Iron and Steel Institute*, 1892, Vol. 1, No. 2.

[3] *J. S. C. I.*, 1903, **22**, 187.

The zero point of M is at the outer side of the stop-cock N so as to secure complete exclusion of all reagents from M. The levelling tube L has a stop-cock communicating with the atmosphere at the top, and near the bottom it communicates with M by a tube so bent that if any air bubbles rise from the lower part of L they are prevented from rising into M. The lower end of L is connected, outside the water jacket, to a T-piece, one branch of which has a stop-cock and leads to the mercury reservoir, while the other is prolonged across the table to a point near the reading telescope, where it terminates in a thick piece of india-rubber tubing compressed by a screw clip having a broad bearing surface. This is used as a fine adjustment when levelling the mercury. The graduations on M are on the side next the telescope, and the stop-cocks are worked from the opposite side in order to secure compactness in the design of the apparatus. The graduations are illuminated by an electric lamp behind a ground glass screen (not shown in fig.) which is placed opposite the telescope.

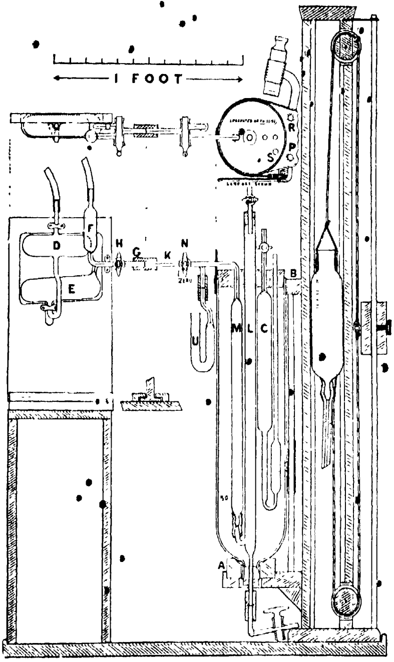

FIG. 102.

The reagents are contained in detachable absorption pipettes each mounted on a wooden stand. The lower bulb E is of about 80 c.c. capacity and is inclined so that the unabsorbed gas may readily be returned to M without tilting the whole apparatus. The reagent is contained in E over mercury, and the upper bulb D takes the mercury displaced when gas is passed into E. The vertical pipette F contains clean mercury, and by means of the three-way stop-cock H, either E or F may be connected with the capillary K. Reference must be made to the original paper for details of the explosion pipette and the special pipette containing phosphorus for the absorption of oxygen. Both embody the mercury pipette F and the three-way stop-cock H.

A feature of this apparatus is the relatively small amount of mercury required. An absorption analysis is carried out as follows: Water is aspirated out of U, to displace air from the capillary tube in connection with it, and air is expelled from M, the capillary K being filled with mercury. The vessel containing the gas sample is connected to G and a sample drawn over into M. The cock M is closed and the volume of gas read off after adjusting the mercury level in L (this vessel being open to the atmosphere). At the same time the reading on the correction tube is taken; this as explained already, gives a percentage correction for temperature and barometric pressure. It is convenient to enter the readings thus:—

Reading.	Correction.	Corrected Reading.
49·97 c.c.	+ 0·04 per cent.	49·99 c.c.

The absorption pipette is placed in position and a little water is aspirated from U into F; mercury is allowed to run back from F to U to fill the capillaries. The gas is passed from M to bulb E, followed by just sufficient mercury to clear the capillary, and the pipette is shaken with the stop-cock closed until absorption is complete. A few more drops of mercury are passed from M to E to expel all reagent from the capillary between H and E. Before returning the gas to M for re-measurement, the soiled mercury in the capillary is returned to U, and when the gas reaches the stop-cock N the latter is turned to deliver the gas into M. The reagent is stopped when it reaches the stop-cock H, and the capillary is cleared of gas by means of clean mercury from F, this being stopped as soon as it reaches N.

While disconnecting the absorption pipette at G it is advisable to place K in communication with U. Any drops of mercury escaping when the rubber tube is removed may be caught in a porcelain basin.

In case of accident the measuring tube may be washed out during the analysis while the gas is in one of the pipettes.

If, as in the determination of carbon monoxide, it is necessary to subject the gas to more than one treatment with an absorbent, the first pipette is disconnected at G and connected direct to the second pipette in order to avoid unnecessary fouling of the capillary K.

Haldane's Apparatus.—This apparatus is widely used for the examination of mine air, and the measuring burette is so arranged that small quantities of carbon dioxide, carbon monoxide, hydrogen and methane can be determined with a high degree of accuracy. Fig 103 shows the laboratory form of apparatus, which is briefly described below.

A slightly modified portable apparatus is also in general use, and is described in Haldane's *Methods of Air Analysis*, 1918, p. 48, which should be consulted by those especially interested in this subject.

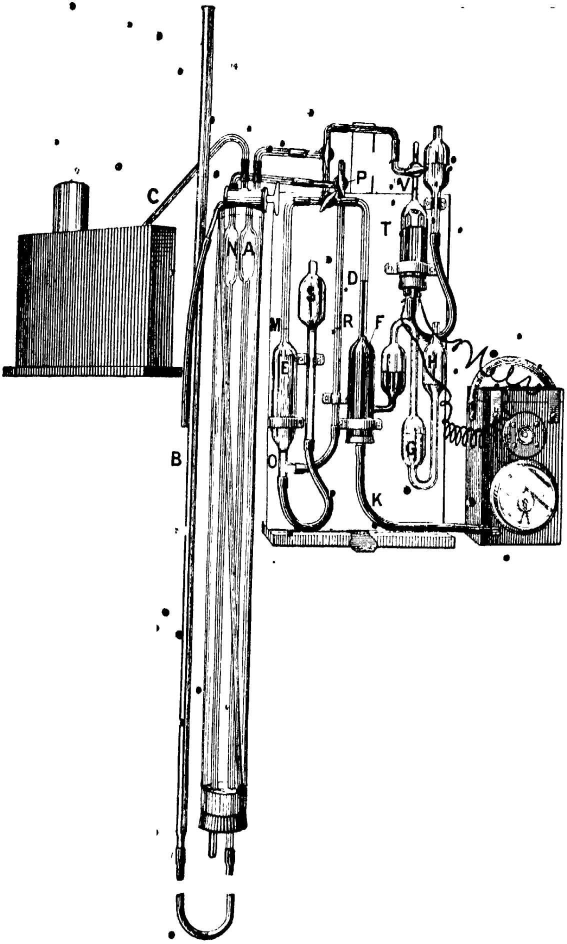

FIG. 103.

The sample of air is collected in a 2 oz. stoppered bottle which will contain enough for three analyses. The stopper is greased with vaseline and during transport held in position by an elastic band. Having regard to the degree of accuracy required in the determination of CO_2, particular attention should be paid to the cleansing and drying of the sample bottle. When collecting the sample a piece of rubber tubing is introduced into the bottle and air is aspirated through the tube so that the bottle is completely washed out by the mine air, care being taken that the sample is not contaminated by the near presence of persons or lamps. To introduce the sample to the apparatus, the bottle is inverted in the mercury trough and the stopper removed under the surface of the mercury by means of a pair of crucible tongs. Then the sample may be drawn into the burette through the curved tube C. The measuring burette A is 800 mm. long and the upper wide portion has a capacity of 15 c.c. The lower narrow portion is 3·5 mm. in bore and is graduated to 0·01 c.c. from 15 to 21 c.c., so that it is possible to read the gas volume by eye estimation to 0·001 c c. or with an accuracy of 0·005 per cent. The burette is surrounded by a water-jacket, the water in which is frequently stirred by blowing air through a tube passing to the bottom. The three-way tap at the top of A gives connection with the tube C and with either of the absorption pipettes E and F or the combustion pipette T. The pipette E contains a caustic potash solution for the absorption of CO_2 and F contains alkaline pyrogallate for the absorption of oxygen, the small pipettes G and H contain caustic potash solution in order to protect the pyrogallate from the atmosphere. The pressure in the measuring burette is adjusted by using the pipette E as a pressure gauge, and bringing the potash to the mark M before reading the burette. This gives a greater degree of accuracy owing to the lower specific gravity of the potash solution compared with that of mercury.

The operation of the compensating or control tube N has been explained on p. 527. By means of this device the readings of the burette are independent of changes of temperature and barometric pressure during the analysis. The combustion pipette T contains a spiral of fine platinum wire which can be raised to a white heat by the passage of an electric current; by this means any combustible gas present in the sample under examination may be completely burnt. The current required may be obtained from a 4-volt accumulator and is led to the spiral through the two glass tubes shown, which are open above but sealed below and filled with mercury. Through the closed end two pieces of stout platinum wire pass. The ends of the spiral are thrust into the open ends of the glass tubes under the mercury surfaces) in such a manner that the spiral can easily be replaced should it be accidentally fused.

This method of determining small quantities of combustible gases presents the considerable advantage that, where the volume of combustible gas present is insufficient to form a satisfactory explosive mixture, it is not necessary to add hydrogen or electrolytic gas as is the case when the forms of apparatus previously described are used.

At the commencement of an analysis it is necessary to have the capillary connecting tubes filled with nitrogen, and for this purpose the nitrogen left at the end of a previous analysis may be employed The pyrogallate, mercury, and potash solution are successively brought to the marks D, V R, and M. The tap connected with the control tube is then closed to the atmosphere. The excess of nitrogen present in A is completely expelle hrough C, and the sample under investigation may then be measured of in A. The carbon dioxide is absorbed first, and as the mercury cannot be allowed to pass beyond the tap on the burette it is necessary to draw the sample backwards and forwards two or three times to clear any CO_2 from the connecting tube.

If the sample is known to contain only traces of combustible constituents the combustion is carried out in the pipette T without any dilution of the sample. The contraction on combustion is noted, and the carbon dioxide formed is absorbed. The residual oxygen is absorbed in the pyrogallate pipette F. If it is required to know accurately the oxygen content of the sample, a separate analysis, in which the combustion is omitted, must be performed, and this enables the oxygen consumed in the combustion to be calculated by difference. The percentages of methane, hydrogen, and carbon monoxide are then calculated as explained earlier in this section. In many samples of mine air, methane is the only combustible present; when this is the case the analysis is considerably simplified, as the oxygen used up in the combustion of the methane may be calculated and added to the residual oxygen found by absorption.

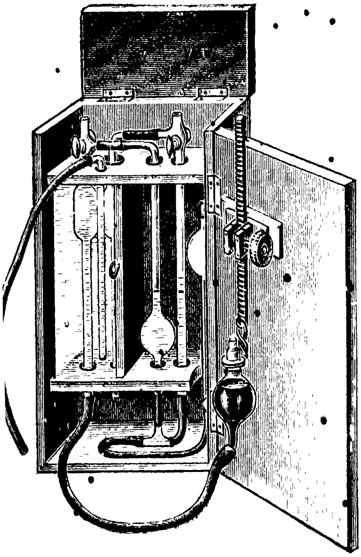

FIG. 104.

If the sample has been taken from any position in which much methane or other combustible was present it must be diluted with air before combustion. In such a case the nitrogen present from the last analysis should be passed into the explosion pipette. A sample of gas is taken for a preliminary estimation of CO_2 and O_2, so that the amount of methane present may be approximately estimated. Quantities of air and gas are then chosen which will give not more than 6 per cent. methane in the mixture. (At least 15 c.c. of one constituent must be taken in order to secure accurate measurement.) Before the air and gas are measured, the residual gas from the preliminary analysis is swept from the apparatus by means of air, after which the connecting tubes are cleared of air by means of the nitrogen previously stored in the combustion pipette. The necessary quantity of air is drawn into the burette, deprived of CO_2 and measured; this is stored in the potash pipette whilst the gas is drawn into the burette and approximately measured. (Before this is done air must be expelled from the tube C by means of mercury from A.) The air is returned to the burette and the mixture measured; the accurate volume of gas taken is obtained by difference. The analysis and calculation of results then presents no peculiar difficulty.

Although particularly designed for the examination of mine air, a little consideration will show that this apparatus has a very general application in cases where it is required to determine with an accuracy of 0·005 per cent. to 0·01 per cent. a particular gaseous constituent which is greatly diluted by air or some other gas.

Fig. 104 shows a simplified form of the apparatus which is intended for the determination of small quantities of carbon dioxide only. The combustion and pyrogallate pipettes are eliminated, and the manipulation of the measuring burette, potash pipette and compensating tube is substantially as described above.

SIMPLER METHODS OF GAS ANALYSIS.

The forms of apparatus previously described are adapted to secure the highest degree of accuracy without special regard to the time involved in carrying out the analysis. For the purposes of controlling industrial operations many less elaborate forms of apparatus have been devised, in which simple analyses can be carried out with great rapidity and in the manipulation of which no high degree of skill is required. Many of these instruments have been arranged to meet the requirements of particular industries and only a few can be described in these pages.

The Orsat-Lunge apparatus is perhaps the most generally used in technical practice. It consists (see fig. 105) of a water-jacketed burette of 100 c.c. capacity attached, as shown, to four pipettes, three of which contain absorbents for carbon dioxide, oxygen, and carbon monoxide respectively and which are filled with glass tubes or rods to present a greater surface of reagent to the gas; the fourth pipette contains water only and is used in conjunction with a tube containing asbestos impregnated with palladium and heated by means of a small spirit lamp. The burette and the reservoir to which it is attached contain acidulated water coloured with methyl orange so that indication is at once given of any accidental fouling with reagents. The sample of gas is drawn into the apparatus through the filter shown on the outside of the apparatus (this may be disconnected when working with gases free from dust), and through the three-way stop-cock. If the gas to be sampled is at less than atmospheric pressure the sampling tubes and filter are filled with a true sample of gas by the operation of the rubber aspirator shown, before the stop-cock is put in connection with the measuring burette. The first sample of gas drawn into the burette is discarded, being employed to drive all air from the capillary connecting tubes. The reagent in each pipette is adjusted to a datum line just below the rubber connection and under no circumstances must any reagent be drawn above the tap. The method of carrying out the absorption is too obvious to need any further description. The temperature conditions for the fractional combustion of hydrogen in the palladium tube have already been stated. Two-thirds of the contraction on combustion represents the hydrogen percentage.

Sodeau[1] introduced another modification of Orsat's apparatus shown in fig. 105 which was especially intended for the examination of products of combustion. He found that the absorption of carbon monoxide in the original Orsat pipette was not completely satisfactory and that the capillary combustion tube containing palladiumized asbestos which Lunge introduced was unsuitable for use in stokeholds. The essential modification introduced by Sodeau was the introduction of a combustion pipette very similar in principle to that used by Haldane. Both these pipettes are adaptations of the "Grisoumeter" introduced by Coquillion for the determination of methane in mine air; this apparatus is figured in Lunge's *Technical Gas Analysis*, 1914, p. 267. The combustion pipette C, may be made from the commercial form of Winkler pipette by simply cutting off the U tube and sealing on a straight piece of capillary tube of suitable length. An ordinary Hempel pipette for solid absorbents may be altered in a similar manner, the neck at the bottom being closed by a two-hole rubber stopper, through which passes a pair of unlacquered brass electrodes bridged across by a platinum spiral, made by coiling about 4 cm. of platinum wire of about 0·3 mm. diameter around a needle 1·3 mm. thick. When the combustion pipette is employed with mixtures rich in combustible gases, the coil must be near the top of the bulb in order that serious explosions may be avoided, but for the analysis of any ordinary chimney gases the coil may be placed much lower in order to reduce the heating of the glass. The gas may then be returned as soon as the current is cut off, without waiting for the glass to cool.

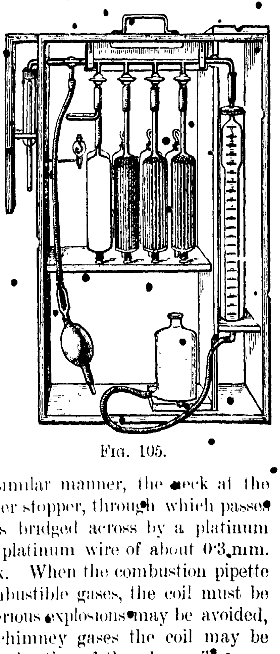

FIG. 105.

A fixed bulb,[2] as in the Hempel (or Orsat) pipette, may be employed to receive the displaced water, unless it is desired to carry out the rapid determination of carbon monoxide and hydrogen together, as described below, when the bulb C should be connected by means of india-rubber tubing to the reservoir CR, consisting of a small aspirator bottle similar to that connected to the measuring tube. When in use, the spiral is raised to a white heat by means of an accumulator, the current being suitably adjusted. In order to eliminate parallax the measuring tube is read by means of a lens sliding on a glass rod. Before each reading is taken the water in the measuring tube is allowed to drain for one minute.

---

[1] *Chem. News*, 1904, **89**, 61.

[2] The ordinary Hempel pipette is sometimes supplied with a bulb too small to contain the water displaced by the heated gas.

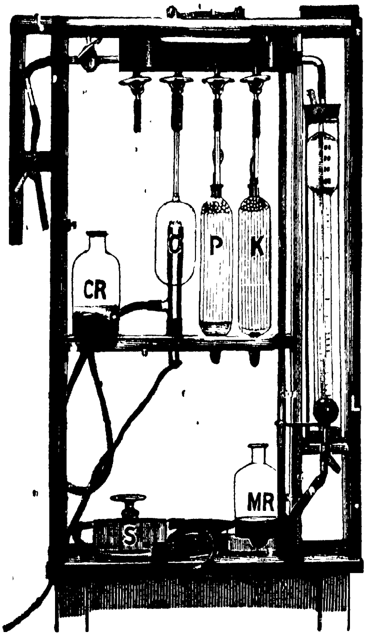

FIG. 106.

The pipettes K and P are of the ordinary Orsat pattern and contain absorbents for carbon dioxide and oxygen respectively.

The U tube filled with glass wool ordinarily supplied with the Orsat apparatus being somewhat apt to clog if dense black smoke is present, it is conveniently replaced by a simple T piece having a small plug of glass wool in the limb through which the sample enters the apparatus. In this way, only the actual samples are filtered, and the solid particles in the main stream pass direct to the aspirator.

The sample is measured in the usual manner, except that it is convenient to close S instead of pinching the india-rubber tube when adjusting the water to the zero mark prior to bringing the gas to atmospheric pressure.

Carbon dioxide is determined by sending the greater part of the gas over into K and back again, then leaving it for one minute to complete the absorption and measuring again as usual; the decrease gives the percentage of carbon dioxide. The current is next switched on, and the gas passed over into the combustion pipette C, where it remains for one minute, being then returned to the measuring tube (after switching off the current) and the contraction noted. The carbon dioxide produced is then determined by a one minute absorption in the potash pipette K; the decrease gives the percentage of carbon monoxide.

As carbon monoxide unites with half its volume of oxygen to form its own volume of carbon dioxide, it follows that to determine the hydrogen percentage half the amount of the carbon monoxide found must be deducted from the contraction during combustion, and two-thirds of such corrected contraction equals the percentage of hydrogen.

For example, if the contraction on combustion amounted to 2·3 c.c. and the resulting carbon dioxide to 1·6 c c., then the gas contained 1·6 per cent. of carbon monoxide and

$$\frac{2}{3}\left(2\cdot3 - \frac{1\cdot6}{2}\right) = \frac{2}{3} \times 1\cdot5 = 1\cdot0 \text{ per cent. of hydrogen.}$$

It should be noted that the only absorbent employed is one which is readily obtained and needs renewing only very infrequently. The determination of carbon dioxide, carbon monoxide, and hydrogen by the above method can be completed in 15 minutes. Any trace of hydrocarbons, if present, will, of course, appear partly as carbon monoxide and partly as hydrogen in the above method of analysis.

It may occasionally be desirable to know the percentage of oxygen originally present in the gas. This may be found by finally absorbing with phosphorus or pyrogallate in the pipette P, and adding to the result the amount of oxygen required to burn the combustible gases.

Rapid Joint Determination of Carbon Monoxide and Hydrogen.—This may be carried out by omitting the measurement immediately after combustion, and transferring the gas direct from C to K in the following manner: After the carbon dioxide has been determined, open the stop-cock attached to C, and switch on the current, raising the reservoir MR, so as to drive the gas into C. Close S when the water has risen to the top of the measuring tube, and, about one minute later, switch off the current and open the stop-cock of K, raising the reservoir CR, so as to drive the gas over into the potash, and finally closing the stop-cock of C. After allowing one minute for absorption, the stop-cock S is opened, the residue drawn back into the measuring tube, and the stop-cock of K then closed. Two-thirds of the contraction so produced equals the percentage of "combustible gases," i.e. carbon monoxide and hydrogen, in the sample.

When collecting samples of chimney gas for subsequent analysis, the sometimes troublesome process of saturating water with the gas to be sampled during the trial may be avoided by appropriately diluting a saturated solution of carbon dioxide. Thus, if the gas is expected to contain about 12 per cent. of carbon dioxide, the sample bottles should be filled with a mixture of 7 parts tap-water and 1 part of water saturated with carbon dioxide.

Further modifications of the original Orsat apparatus are described by Lunge (loc. cit., 66-81).

Hempel's Apparatus.—This apparatus is extremely simple in construction and is widely used for analyses in which only a moderate degree of accuracy is required. Full details of this and other simple forms of gas apparatus will be found in Hempel's *Gas Analysis*. A brief description of some of the apparatus follows.

The Gas Burette.—This consists of two tubes of glass mounted on feet, one tube being graduated to 100 c.c. in $\frac{1}{5}$ c.c. (the burette proper), and the other plain (the pressure tube). They are connected at the feet by rubber tube, much in the same way as Lunge's nitrometer. The arrangement is shown in fig. 107.

The illustration shows the burette with three-way stop-cock at bottom, which is necessary in the case of gases soluble in water. If this is not the case, a burette without such stop-cock is substituted (fig. 108). The rubber tube should not be in one piece but of two pieces connected in the middle by a short length of glass tube to admit of being readily disconnected.

Fig. 108 illustrates not only the original Hempel burette with pressure tube, but also the method of connection with the gas pipette, and the way in which the rubber tube is joined by the intervening glass tube. The compensating device for temperature and pressure due to Hempel and described on p. 526, is incorporated in the later form of Hempel burette.

Hempel, with great ingenuity, has devised special pipettes to be used in connection with the burette, which render the instrument very serviceable for general gas analysis. The pipette shown in fig. 108 is known as the simple absorption pipette, and serves for submitting the gas originally in the burette to the action of some special absorbent. With a series of these pipettes the gas is submitted to the action of special absorbents, one after another, until the entire composition is ascertained. The connections must in all cases be made of best stout rubber, and bound with wire.

Collection and Measurement of the Gas over Water.—Both tubes are filled completely with water (preferably already saturated mechanically with the gas), care being taken that all air is driven out of the rubber tube. The clip is then closed at the top of the burette and the bulk of the water poured out of the pressure tube, the rubber tube being pinched meanwhile with the finger and thumb to prevent air entering the burette. The latter is then connected by a small glass tube with the source of the gas to be examined, when, by lowering the pressure tube, the gas flows in and displaces the water from the burette into the pressure tube. The pressure is then regulated by raising or lowering either of the tubes until the water is at the same level in both, when the volume of gas is read off. It is convenient, of course, to take exactly 100 c.c. of gas to save calculation.

Collection and Measurement of the Gas without Water.—In this case the three-way tap burette (fig. 107) is dried thoroughly by first washing with alcohol, then ether, and drawing air through it. The three-way tap is then closed, the upper tube connected with the gas supply, and the burette filled either by the pressure of the gas or by using an aspirator bottle attached to the three-way cock to draw out the air and fill the burette with gas. The air may be expelled from the aspirator which is subsequently filled with gas so that the pressure in the burette may be adjusted to that of the atmosphere. The taps are then turned off, and connection made with the pressure tube, which is then filled with water, and the tap opened so that the water may flow into the burette and absorb the soluble gases present. As the burette holds exactly 100 c.c. between the three-way tap and the upper clip, the percentage of soluble gas is shown directly on the graduation.

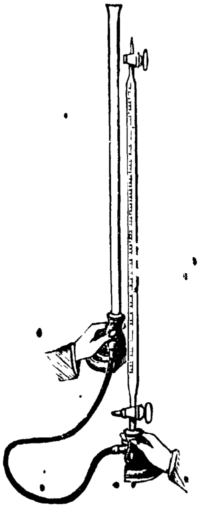

FIG. 107.

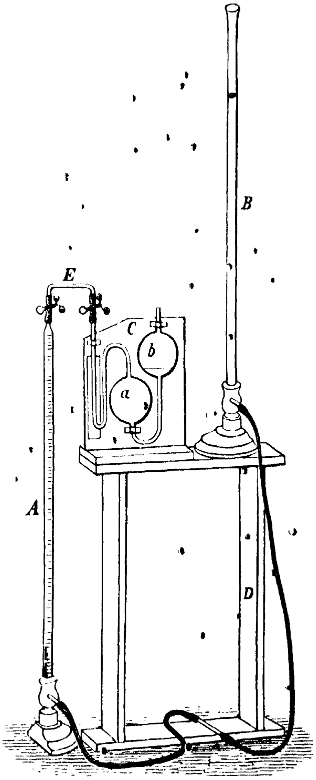

FIG. 108.

The Method of Absorption.—In the case of the simple pipette (fig. 108), *a* is filled with the absorbing liquid, which reaches into the siphon bend of the capillary tube; the bulb *b*, remains nearly empty. In order to fill the instrument, the liquid is poured into *b*, and the air sucked out of it by the capillary tube. It is convenient to keep a number of these pipettes filled with various absorbents, well corked and labelled.

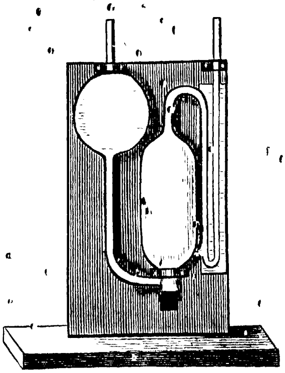
FIG. 109.

Another pipette of similar character is shown in fig. 109, and is adapted for solid reagents, such as stick phosphorus in water. The instrument has an opening at the bottom, which can be closed with a rubber stopper. This pipette is also used for absorbing CO_2 by filling it with plugs of wire gauze and caustic potash solution so as to expose a large active surface when the liquid is displaced by the gas.

To make an absorption, the capillary **U** tube is connected with the burette containing the measured gas by a small capillary tube E (fig. 108), the pinch-cock of course being open, then by raising the pressure tube, the gas is driven over into the cylindrical bulb, where it displaces a portion of the liquid into the globular bulb. When the whole of the gas is transferred, the pinch-cock is closed, and the absorption promoted by shaking the gas with the reagent. When the action is ended, communication with the burette is restored, and the gas siphoned back by means of the pressure tube into the burette, to be measured.

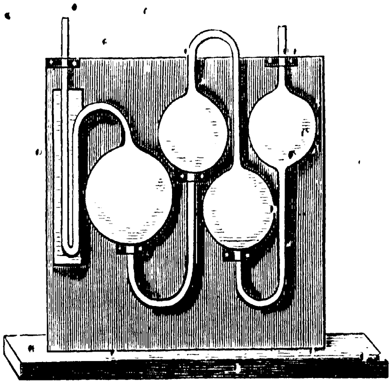
FIG. 110.

The Double Absorption Pipette, shown in fig. 110, is of great utility in preserving absorbents which would be acted on by the air, such for instance as alkaline pyrogallate, cuprous chloride, etc. The bulb on the left is filled with the absorbent, the next is empty, the third contains water, and the fourth is empty. When the gas is passed in, the intermediate water passes on to the last bulb to make room for the gas, thus shutting off all contact with the atmosphere, except the small amount in the second bulb. An arrangement is also made for the use of solid reagents, by substituting for the bulb on the left a cylindrical bulb as in fig 109.

Hydrogen Pipette.—The hydrogen gas necessary for explosions or combustions is produced from a hollow rod of zinc fixed over a glass rod passed through the rubber stopper (fig. 109). The bulb being filled with dilute acid, gas is generated, and as it accumulates the acid is driven into the next bulb and the action ceases.

Explosion Pipette.—Another arrangement provides for explosions by the introduction into a thicker bulb of measured volumes of the gas, of air, and of hydrogen. The bulb being shut off with the stop-cock, a spark is passed through wires sealed into the upper portion of the bulb.

Pipette for Fractional Combustion.—This consists of a simple pipette to which is attached a capillary tube containing palladiumized asbestos for the combustion of hydrogen and carbon monoxide in a manner similar to that described in connection with the Orsat-Lunge apparatus.

Bedson's Arrangement of Pipettes.—This is used in connection with Dittmar's apparatus, but may be adapted to fit other types. The pipettes are shown in fig. 111. A capillary tube with a three-way stopcock A is fused to the Hempel pipette the capillary is drawn out and bent so as to pass into the mercury trough. The tap A can be placed in connection with C to which is attached a moveable mercury reservoir D. In working, e.g. transferring gas to E, the absorbent fills E and the capillary of tap A. By raising D, the vessel C and capillary B are entirely filled with mercury. B, of course, is immersed in the mercury trough. Having filled B with mercury, the test tube containing gas to be examined is brought over the end of B and some gas drawn into C by lowering D. The tap is then turned to put the tube in connection with E, and the gas forced into E, by depressing the tube in the trough. By raising and lowering the tube, the gas can be brought into intimate contact with the absorbent and absorption thus promoted. To bring all the gas into E, D is again used and the remaining gas drawn into C by lowering D; then

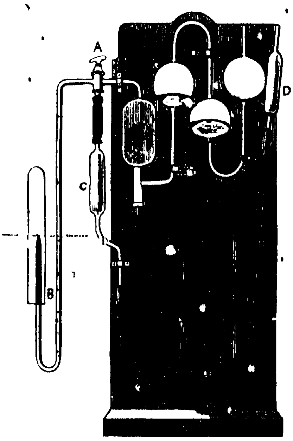

Fig. 111.

by turning the tap, the gas from C can be forced into E; the tap is then turned so as to put the capillary and E in connection, and the gas flows into E with a small portion in capillary B, retained by the column of mercury filling the bent limb.

The gas may be left thus for some hours; and, to transfer it to the tube, C and E are placed in connection by suitably turning the tap; then by lowering D some gas is drawn into C and the tap turned so as to put C and the tube in connection. By carefully raising D the mercury is washed out of B and some of the gas passes into the tube. With B clear of mercury and filled with gas, the tube and E are placed in connection and the gas flows out of E into the tube. When the liquid from E has risen so as to fill the vessel up to the tap (the capillary of the tap being also filled), the tap is turned to put C and B in connection; then by raising D all gas is washed out of C and the capillary into the tube used for its collection and transferred to the measuring tube.

Bedson also attaches to the measuring apparatus a vessel containing a known volume of air at known temperature and pressure, as recommended by Lunge, so as to dispense with the otherwise necessary corrections.

Many of the absorption pipettes described in the foregoing pages have been modified so that the gas enters the pipette under the surface of the liquid but is drawn off from the top in the usual way. Dennis[1] and Van Alstine[2] have devised apparatus making use of this principle in order to secure very intimate contact between gas and liquid.

CALCULATION OF CALORIFIC VALUE.

Since the heating effect of a combustible gaseous mixture is the sum of the heating effects of the component constituents, the calorific value may be calculated from the volumetric analysis. The accuracy of the computed figure depends, of course, on the accuracy of the analysis, and for this reason it is preferable when dealing with complex mixtures such as coal gas to make a direct determination of calorific value. The reader must be referred to text-books dealing more specifically with the coal gas and fuel industries for descriptions of gas calorimeters; the whole subject is well treated by Coste in *The Calorific Power of Gas.*

The calorific value is usually expressed for technical purposes in B.Th.U. per cubic foot of gas, measured at a temperature of 60° F. and a pressure of 30 ins. mercury, and saturated with water vapour under those conditions. Such values for the commoner combustible gases are given in Table C, together with the corresponding values in calories (K.C.U.) per cubic metre of dry gas measured at 0° C. and 760 mm. Hg. pressure. The values in calories (K.C.U.) per gm. mol. (from which the other figures are calculated) are given in the first column.

In calculating the heat units per unit volume, the experimental weight-volume relationships for the several gases given in Table A have been taken. In many text-books the calorific values appear to have been calculated on the assumption that the molecular volumes of all gases are equal. When calculating the calorific value of a gaseous mixture it is

[1] *J. Ind. Eng. Chem.*, 1912, 4, 898.

[2] *Ibid.*, 1919, 11, 51.

necessary to assume (in the absence of sufficiently reliable data) that the molecular volume of a given gas under standard conditions is the same whatever the partial pressure from which it is deduced.

TABLE C.

CALORIFIC VALUES.

	K.C.U. per Gm Mol	K.C.U. per Cub Metre at 0° C. and 760 mm. Dry.		B.Th.U per Cub. Ft. at 60° F. and 30 Ins. Saturated with water vapour.	
		Gross.	Net	Gross.	Net
Acetylene	310·05	14093	13584	1477	1423
Benzene	776·90	34697	33242	3635	3481
Carbon monoxide . .	67·96	3035	3035	317·9	317·9
Ethane	370·44	16716	15200	1751	1592
Ethylene	333·35	14997	13990	1571	1466
Hydrogen	68·11	3050	2551	319·5	267·2
Methane	213·50	9548	8510	1000	895
Propane	529·21	24257	22315	2541	2336
Propylene	492·74	22698	21151	2378	2216

In the case of coal gas a much more serious error is involved in the assumption of some mean value for the calorific value of the olefines; many chemists take the value for propylene, but, if in the analysis benzene has been absorbed with the olefines, or if the gas consists partly of carburetted water gas, it will be found that this value is too low. Coste (*loc. cit.*, p. 84) recommends that the value for the hydrocarbons absorbed by bromine or fuming sulphuric acid (including benzene and acetylene) should be 670 K.C.U. (2659 B.Th.U.) gross or 600 K.C.U. (2381 B.Th.U.) net per cubic foot (at 60° F. and 30 ins. saturated).

Another slight error is involved when ethane is neglected in the explosion analysis. If a mixture of *a* per cent. H_2, *b* per cent. CH_4, and *c* per cent. C_2H_6 be exploded and, as is a common practice, *a* and *b* are calculated on the assumption that *c* is zero, the figure for *a* will be low to the extent of *c* per cent. and the figure for *b* will be high to the extent of 2*c* per cent.; hence the calculated calorific value will be low to the extent of 0·7*c* B.Th.U. per cubic foot.

DETERMINATION OF GASES BY TITRATION.

Whenever a large sample of gas is available it is usually more convenient, and often more accurate, to resort to the general methods of volumetric analysis in cases where a suitable absorbent is available for the gases to be determined. A few examples of such methods are given below by way of illustration, and the reader must be referred to the earlier sections for guidance in the choice of absorbents and standard solutions to meet particular requirements.

A very simple device is one employed by the Inspectors appointed under the Alkali, etc., Works Regulation Act, 1906, for their routine testing to control the escape of acid and other gases scheduled by the Act as "noxious and offensive gases". The absorbing liquid is placed inside a Fletcher's collapsible rubber bellows whose exact capacity—about $\frac{1}{10}$ cub. ft.—should be periodically determined by drawing air from a glass aspirator and noting the volume of water required to replace the withdrawn air. The absorbent having been introduced, air is expelled from the bellows and the gas sample is drawn in by expansion of the bellows. The gas and liquid are brought into contact by vigorous shaking, and, if desired, further samples of gas can be treated before the liquid is expelled for titration.

The standard solutions employed for titration may be so arranged as to minimize calculations. When determining the escape of acid gases, it is convenient that the burette reading should give directly the equivalent weight of SO_3 in grams per cubic foot of gas when the bellows has been filled five times with gas. In other cases special *normal gas solutions* may be made up. These are of such strength that 1 c.c. of solution represents 1 c.c. of the absorbable gas measured at 0° C. and 760 mm. dry. For instance, a normal gas solution for chlorine would be made up to contain 4·494 gm. of As_4O_6 with a few grams of Na_2CO_3 per litre. The corresponding solution of iodine would contain 11·53 gm. per litre, in order that 1 c.c. of either solution should correspond to 1 c.c. of chlorine gas. The weights of dry gases in grams per litre given in Table A enable the strengths of other normal gas solutions to be readily calculated.

The Fletcher's aspirator described above possesses the advantages of portability and durability, but its application is limited in so far as it is only possible to take intermittent gas samples, and it must not be used for gases or liquids which would be affected by the rubber.

When it is desired to draw a large sample of gas over a period, the absorbing liquid should be placed in a series of gas washing or absorption bottles. The residual gas may be measured by passing through an ordinary gas meter (in which case a water-jet pump must also be used if the gas being sampled is not at a sufficiently high pressure to force the sample through the absorbing liquid and the meter) or by collecting in an aspirator. In either case the pressure and temperature at which the gas is measured should be noted.

The arrangement of the wash bottle, aspirator, and measuring cylinder, as used in the determination of sulphur dioxide, is shown in fig. 112. A suitable quantity of standard iodine solution with a little freshly-made starch solution is placed in the wash bottle and made up to about 150 c.c. with distilled water. The reaction involved is represented by the equation

$$I_2 + SO_2 + 2H_2O = H_2SO_4 + 2HI$$

and the end-point is determined by watching for the disappearance of the blue colour. When dealing with gases containing 5 to 10 per cent. SO_2, 10 c.c. of $N/_{10}$ iodine solution should be taken. This corresponds to 0·03203 gm. SO_2 or to 11·20 c.c. SO_2 measured at 0° C. and 760 mm. dry. (This volume varies slightly according to the percentage of sulphur dioxide in the gas under analysis, as sulphur dioxide shows an appreciable deviation from Boyle's law at low pressures.)

Before carrying out a test, a blank should be performed in order to fill the gas sampling tube with a true sample; also the whole apparatus should be proved gas-tight. The method of aspirating the sample through the wash-bottle being obvious, it need only be mentioned that the gas in the aspirator should be at the same pressure at the beginning and end of the test. The rate at which the gas bubbles through the liquid is controlled by the rate at which water is run from the aspirator.

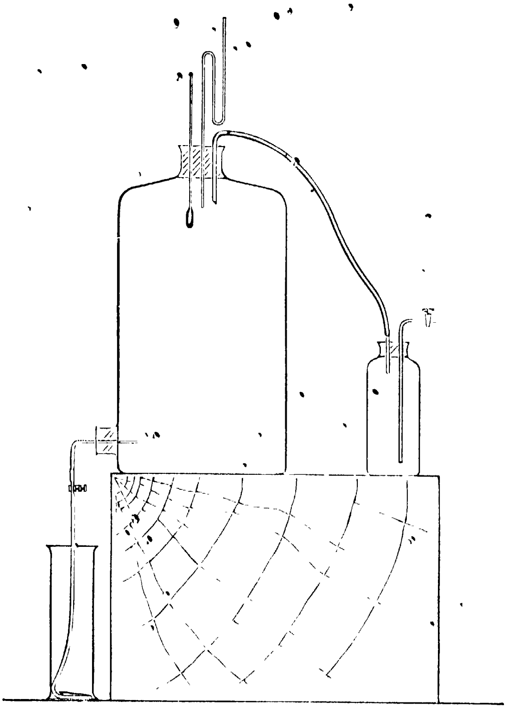

FIG. 112.

Whilst the gas is passing through the absorbent, the wash-bottle should be gently shaken, and to facilitate this the connections to it are made with flexible rubber tubing. The gas stream is stopped immediately the blue coloration disappears; if necessary, water is siphoned back into the aspirator from the measuring cylinder (or vice versa) to adjust the pressure of gas in the aspirator; the net volume of water collected then represents the volume of residual gas drawn through the wash-bottle. This volume is corrected for temperature and barometric pressure, and, if the results are required on a dry basis, for the pressure of aqueous vapour in the aspirator. The corrected volume, added to the volume of sulphur dioxide absorbed, gives the volume of the original sample, from which the percentage of sulphur dioxide is calculated.

The use of iodine is not permissible where it is desired to carry out a test over a long period owing to the error involved by the evaporation of iodine. Lehmann employs a second wash-bottle containing 5 c.c. of $^N/_{10}$ sodium thiosulphate solution through which the gas is passed after passage through the iodine solution; the necessary correction for the evaporated iodine can then be applied. A more convenient method, however, is to use caustic soda as an absorbent.

When carrying out these long-period tests a much larger sample of gas should be taken; a suitable aspirator can be made from a 10-gallon sheet-iron drum, and a more regular flow of gas is obtained if the inlet tube to the aspirator is carried to the bottom, to secure a constant head of water.

Caustic soda is often used as an absorbent for the determination of total acid gases, and by carrying out two titrations it is possible to distinguish between sulphur dioxide and sulphur trioxide in this way. It has been found, however, that when the test is run over a long period a serious error is introduced owing to the oxidation of sodium sulphite. Titoff[1] pointed out that this was due to the presence of minute traces of catalysts and could be prevented by the addition of a negative catalyst. Haller[2] has investigated the methods of determination of sulphur dioxide and recommends the use of glycerin as a negative catalyst to prevent the oxidation. The absorption of sulphur dioxide by caustic soda is very rapid so that any simple form of wash-bottle can be employed.

Ammonia is usually determined by titration after absorption in standard acid The efficiency of this method applied to the analysis of coal gas has been investigated by the U.S. Bureau of Standards (Tech. Paper 34) and the importance of using proper indicators is emphasized. Sodium alizarin-sulphonate, cochineal and paranitrophenol were found to be the most suitable. When carrying out a long period test it is preferable to absorb the ammonia in a large excess of acid and then to distil off the ammonia with caustic soda, as in the analysis of crude ammoniacal liquor.

Determination of the Oxides of Nitrogen.—In the absence of ammonia, nitric oxide and nitrogen peroxide are determined by absorption in standard alkali and titration of the excess of alkali with or without the addition of hydrogen peroxide. Owing to the difficulty of absorbing nitric oxide by water or alkali a large excess of oxygen should be used to ensure oxidation to nitrogen peroxide.

The gas leaving the catalyst of an ammonia oxidation plant contains unoxidized ammonia mixed with the oxides of nitrogen, and in this case the use of an oxidant needs special consideration as hydrogen peroxide and ozone oxidize ammonia to ammonium nitrite. Fox[3] employs the following method for the analysis of this mixture: The gas is mixed with a measured volume of oxygen sufficient for the oxidation of nitric oxide and is then passed through two absorption vessels. The first vessel contains standard alkali only, and absorbs some of the nitrogen peroxide together with all the ammonia (unless present to an abnormal extent). The second vessel contains standard alkali and hydrogen peroxide (the concentration of which should be 1 per cent.) to complete the absorption of nitrogen peroxide. The ammonia in this case is determined by oxidation with sodium hypobromite, and the nitrogen peroxide by separate titrations of the two absorbing solutions. The residual gas after absorption is measured in an aspirator, and, in calculating its volume, allowance must be made for (1) the volume of oxygen added; (2) the volume of water vapour condensed from the gas in the first absorption bottle; and (3) the small volume of oxygen evolved from the hydrogen peroxide; Fox (loc. cit.) gives full details of these calculations and deduces a simple formula for the ratio of nitric oxide to ammonia (which represents the efficiency of the catalytic oxidation process). Taylor and Davis[1] and Gaillard[2] describe different methods which may offer possibilities for development of a rapid method of works control.

---

[1] *Z. Phys. Chem.*, 1903, **45**, 641.

[2] *J. S. C. I.*, 1919, **38**, 52T.

[3] *J. Ind. Eng. Chem.*, 1917, **9**, 737.

Sulphuric acid is an efficient absorbent for mixtures of nitric oxide and nitrogen peroxide and the solution may be titrated with potassium permanganate, making use of the following reactions:

$$10NO + 6KMnO_4 + 9H_2SO_4 = 10HNO_3 + 3K_2SO_4 + 6MnSO_4 + 4H_2O$$
$$5N_2O_3 + 4KMnO_4 + 6H_2SO_4 = 10HNO_3 + 2K_2SO_4 + 4MnSO_4 + H_2O$$
$$10NO_2 + 2KMnO_4 + 3H_2SO_4 + 2H_2O = 10HNO_3 + K_2SO_4 + 2MnSO_4$$

When it is required to differentiate between the oxides, it is necessary to determine whether excess oxygen is present, and to determine the total nitrogen in a nitrometer.

Nitrous Oxide is determined by combustion with hydrogen in the Drehschmidt platinum capillary heated to bright redness. Pollak[4] uses carbon monoxide instead of hydrogen for the combustion and calculates the nitrous oxide from the carbon dioxide produced. Mixtures of nitrous and nitric oxides may be similarly determined if the contraction is ascertained. Knorre and Arndt determined nitric oxide by combustion with hydrogen, but as ammonia may be formed under certain conditions the use of carbon monoxide is preferable.

The reactions involved in Pollak's method are

$$2NO + 2CO = 2CO_2 + N_2 \qquad \text{Contraction} \quad 0{\cdot}5 \text{ Vol. NO.}$$
$$N_2O + CO = CO_2 + N_2 \qquad \text{Contraction} \quad \text{Nil.}$$

The Determination of Hydrocyanic Acid.—The most accurate determinations of hydrocyanic acid in coal gas are obtained by the thiocyanate method, which is carried out as follows. The gas is passed at a rate of about 1 cub. ft. per hour through a train of three wash bottles containing a solution of ammonium sulphide and free sulphur. After passage of a suitable volume of gas, the contents of the three bottles are washed out into one vessel and made up to a known volume. The thiocyanate is determined by silver nitrate titration as in the analysis of ammoniacal liquor, the HCN value being calculated from the relation

---

[1] *J. Ind. Eng. Chem.*, 1917, **9**, 1106. [2] *Ibid.*, 1919, **11**, 745.

[3] Knorre and Arndt, *Ber.*, 1899, **32**, 2136.

[4] Treadwell and Hall, *Analytical Chemistry*, 5th. ed. 1919, Vol. 2, p. 802.

$$1 \text{ c.c. } {}^{N}/_{10}\ AgNO_3 \equiv 0{\cdot}007612 \text{ gm. } NH_4CNS \equiv 0{\cdot}002703 \text{ gm. } HCN.$$

The amount of hydrocyanic acid in gas can also be readily determined by the method recommended by Nauss,[1] in which the gas is passed through a train of two wash bottles, each containing 20 c.c. of ferrous sulphate solution (1 part salt to 10 parts of water) and 20 c.c. of KOH solution (1 part KOH to 3 parts of water). The gas is passed through at a rate of about 1 cub. ft. per hour. About 100 litres of gas are passed through in from two to three hours and the contents of the wash bottles washed out and made up to 500 c.c. in a flask. The ferrocyanide in this solution is determined by titration with copper or zinc sulphate.[2]

It may be remarked that the thiocyanate method tends to give results slightly above the correct value, owing to the fact that the ammonium polysulphide absorbs at least a part of any carbon bisulphide present in the gas, ammonium thiocarbonates being formed, and these may undergo subsequent decomposition yielding ammonium thiocyanate. The ferrocyanide method, on the other hand, is liable to yield low results owing to small quantities of hydrocyanic acid being converted into thiocyanide instead of ferrocyanide, this effect being accentuated when the gas contains ammonia.

The Determination of Carbon Bisulphide in Coal-Gas.—Harcourt determined CS_2 in coal-gas by aspirating a known volume of the gas over platinized pumice heated to 420° C., whereby the CS_2 is converted to H_2S. The H_2S was determined colorimetrically by absorption in a solution of lead syrup. If desired, the test may be run over a longer period and the H_2S absorbed in NaOH solution.

For most purposes in gas works practice, it is not necessary to differentiate between CS_2 and other sulphur compounds (excepting of course H_2S) For determination of the total sulphur the method of the Gas Referees is the most accurate; full details of this will be found in the *Notification of the Gas Referees* and in many text-books on Gas Works chemistry. The gas is burnt in a special burner surrounded by ammonium carbonate; the products are condensed and the sulphur is finally precipitated and weighed as $BaSO_4$.

Somerville[3] devised a method which rapidly gives results with approximate accuracy. A known volume of gas is burnt and the products aspirated through iodine solution, SO_2 being determined as described on p. 574.

The Determination of Benzol in Gas.—The most suitable method for the accurate determination of benzol, etc., in coal gas is that devised by Déville[4] and recently modified by him so as to make it applicable to gases containing very small quantities of benzol.[5] The method consists in condensing crude benzol from dry gas and submitting the condensate to distillation tests. When the gas contains only a small proportion of benzene it is dried by passing over calcium chloride, and then cooled to – 72° C. by passing through a condenser immersed in carbon dioxide snow in a Dewar flask. At this temperature the vapour pressure of benzene (and *a fortiori* of other aromatic hydrocarbons) is practically nil. Thus all the vapours are condensed, and the residual gas may be measured by means of an ordinary meter ; the weight of crude benzol per unit volume of gas measured at 10° C. and 760 mm. pressure is calculated after allowing for the volume of vapour condensed ; this is assumed to be 1 litre per 3·73 gm. (based on 3 vols. benzene + 1 vol. toluene). The composition of the crude benzol is estimated by any of the well-known fractional distillation methods.

---

[1] *J. Gas Lighting*, 1900, **76**, 960.

[2] Knublauch, *J. Gasbeleuchtung*, 1889, **33**, 450; Skirrow, *J. S. C. I.*, 1910, **29**, 319; Colman, *Analyst*, 1908, **33**, 261; *ibid.*, 1908, **33**, 265.

[3] *J. Gas Lighting*, 1910, **112**, 28.

[4] *Journal des Usines a Gaz*, 1889.

[5] *Journal des Usines a Gaz*, 1918; *Gas Journal* 1919, **145**, 272.

When dealing with a good quality "straight coal gas" it is not necessary to cool to such a low temperature In this case the benzol condensed at a temperature of – 21·7° C. by means of ice and salt is determined as above, and, to the result obtained a constant correction of 23·5 gm. per cub. metre is added to allow for the vapour pressure of benzene at – 21·7° C.

H. S. Davis and M. D. Davis[1] describe a differential pressure method for the quantitative determination of vapours in gases. The method involves the use of two flasks connected to a delicate differential pressure gauge. One flask is filled at atmospheric pressure with gas containing the vapour whose amount is to be determined. The other flask is filled at the same pressure with gas from which the vapour is absent. The gas in each flask is now saturated with the vapour and the differential pressure developed is indicated by the gauge, and gives directly the partial pressure of the vapour originally in the gas.

Another method of determination, which is widely used in connection with the control of benzol extraction plants, consists in the absorption of benzol by means of creosote or other oil of low volatility and the subsequent steam distillation of the oil for the isolation of crude benzol. Rhead[2] describes a suitable washing tower for this purpose which contains a number of trays. Oil enters the top tray from a constant-head feed, gravitates from tray to tray through sealed pipes, and finally collects in a receiver at the base of the tower. The gas, after passing through a meter, is passed upwards through the tower and is caused to bubble through the oil in each tower by means of hoods with serrated edges. About four litres of oil are required to extract the benzol and toluol from 100 cub. ft. of coal gas. The use of some apparatus for extraction such as the above, embodying the counter-current principle, offers considerable advantage compared with the use of a series of wash-bottles, owing to the back pressure caused by the oil and to the need for having fresh oil for removing the last traces of benzol in the latter case. Lessing[3] packs a scrubbing tower with pieces of inert material (e.g. porous brick) soaked in an oil of such viscosity that it is not unduly thinned or washed out by the solvent vapours from the gas. This tower offers little resistance to the flow of gas, and the arrangement admits of the benzol and other vaporous constituents being recovered by steam distillation from the tower itself without removal of the absorbent. Gray[1] describes an arrangement in which the gas to be washed passes through a mass of condensing vapour.

---

[1] *J. Ind Eng Chem.*, 1918, **10**, 709

[2] *J. S. C. I.*, 1917, **36**, 767.

[3] *Ibid*, 103.

Lebeau and Damiens[2] and Burrell, Siebert and Robertson[3] employ methods depending upon the fractional distillation of liquefied coal gas for the examination of vaporous constituents. Such methods are particularly applicable for the determination of some of the compounds present in coal-gas to a small extent (e.g. thiophen) which may be condensed and subsequently held in solution by the benzol or by some other added solvent.[4]

Pfeiffer[5] determines benzene by treating a known volume of the gas contained in a separating funnel with sulphuric and nitric acids. The resulting dinitrobenzene is titrated with stannous chloride.[6]

Determination of Naphthalene in Coal-Gas.—A method was proposed by Leather[7] for the determination of naphthalene in coal-gas in which large volumes of the gas (200 to 300 cub. ft.) are passed slowly through pure benzene, the latter being then carefully evaporated. In addition to naphthalene—toluene, xylenes, etc., are extracted from the gas in the process, and, although separation of the naphthalene from these bodies can be effected by careful fractional distillation, the process is cumbersome and requires very considerable time. The amount of naphthalene in coal-gas is now determined by the method introduced by Colman and Smith[8] which depends on the fact that naphthalene combines with picric acid to form a fairly stable crystalline compound $C_{10}H_8 . C_6H_3N_3O_7$, this being scarcely soluble in aqueous picric acid. The precipitate so formed does not, however, consist of pure naphthalene picrate but is a mixture of the latter with varying quantities of free naphthalene. The difficulty so introduced into the determination was overcome by Colman and Smith by treating the precipitate in the manner due to Kuster[9] and used by him for the determination of naphthalene when mixed with other solid hydrocarbons which do not form stable compounds with picric acid. Colman and Smith[10] have slightly modified their original method. The gas is passed through a series of four wash bottles, the first of glass throughout—containing a 10 per cent. solution of citric acid to retain any ammonia in the gas. The second contains 100 c.c. of $^{N}/_{20}$ picric acid, and the third 50 c.c. of the same solution, the last being empty to retain spray. It is important that prior to and during its passage through the train of wash bottles, the gas should not have access to india-rubber. It has been shown that a length of about 18 ins. of india-rubber is sufficient to absorb the whole of the naphthalene from gas containing 6 to 10 grains per 100 cub. ft. when the latter passes at the rate of from 0·5 to 1 cub. ft. per hour.[1] The picric acid solution is standardized with $^N/_{10}$ caustic soda solution, lacmoid or phenolphthalein being used as indicator. The gas (about 10 cub. ft.) is passed through the apparatus at a rate not exceeding 1 cub. ft. per hour, the volume being corrected to N.T.P. (generally 60° F. and 30 ins. pressure). After passage of the gas, the contents of the third and fourth bottles of the train are washed into the second bottle, which is then closed with a tight-fitting rubber stopper fitted with glass stop-cock or similar device. By means of a pump, the wash bottle is evacuated until the precipitate rises to the surface. The stop-cock is then closed and the contents heated to boiling by immersion in a bath with occasional shaking and then allowed to cool, the shaking being continued to prevent sublimation of the naphthalene into the upper region of the bottle. This procedure ensures the conversion of the whole of the naphthalene present into naphthalene picrate. The volume of the cold mixture is measured, the precipitate is separated by filtration through a dry filter paper, the first few c.c. of filtrate being rejected, and 100 c.c. of the filtrate titrated with $^N/_{10}$ NaOH solution. If v c.c. is the difference between the volume of $^N/_{10}$ NaOH required to neutralize the total volume of $^N/_{20}$ picric acid solution originally taken and that required for the neutralization of the total volume of picric acid solution after heating and filtering, then—grains of naphthalene per 100 cub. ft.

---

[1] *J. C. S.*, 1917, **111**, 179.

[2] *Compt. Rend.*, 1913, **156**, 144, 325.

[3] *U. S. Bureau of Mines Tech. Paper*, No. 104, 1915.

[4] Campbell (*Proc. Phys. Soc.*, 1920-21, **33**, 287), has described an electrical method employing the Pirani pressure guage which appears to be especially applicable to the determination of such constituents.

[5] *J. Gasbeleuchtung*, 1899, **42**, 697.

[6] *Limpricht*, *Ber.*, 1878, **11**, 35.

[7] *J. Gas Lighting*, 1899, **73**, 1737.

[8] *J. S. C. I.*, 1900, **19**, 128.

[9] *Berichte*, 1894, **24**, 1101.

[10] *Gas Journal*, 1918, **144**, 231-232.

$$= \frac{v \times 19{\cdot}75}{\text{Volume of gas passed}}$$

Knublauch[2] directs attention to certain points of criticism which have been directed against the Colman-Smith method for napthalene determination. The principal of these is that all the naphthalene is not precipitated in the combined form. Moreover, the use of a separate vessel for ammonia absorption prior to the gas entering the solution of picric acid renders the method unsuitable for use with warm gases. Knublauch has investigated such points as, the decomposition of naphthalene picrate by dilute alkali, by water and by cold picric acid, the combination of picric acid with excess of naphthalene, the effect of the benzol and phenol contained in the gas on the titration value of the product, solubility of naphthalene in cold dilute sulphuric acid, etc., and as a result of such investigations has devised two simple methods of naphthalene determination termed respectively the difference and direct titration method. The difference method follows the lines of Colman and Smith's method already described, two vessels containing a 1 per cent. solution of picric acid as naphthalene absorbent being employed. The "direct titration method" is claimed to be a simple and more direct method. The method is applicable to warm gases and no separate vessel for prior absorption of ammonia, cyanogen, phenols, etc., is required. The absorption is carried out in two cylindrical wash bottles. The first contains 110 c.c. of a mixture of picric acid and sulphuric acid made up in the proportion of 40 c.c. of 1 per cent. picric acid solution, 40 c.c. of N sulphuric acid, and 30 c.c. of water. The second wash bottle contains 25 c.c. of a 1 per cent picric acid solution. In the absence of ammonia, 1 per cent. picric acid solution is employed alone. In these latter circumstances, from 50 to 55 litres of coal gas are passed through the wash-bottles, and when sulphuric acid is used in addition to picric acid (i.e. in presence of ammonia) from 80 to 85 litres of gas are employed. Towards the end of the absorption a small amount of picrate is formed in the second vessel. The whole of the precipitate is transferred to a filter and washed with a 0·2 per cent. picric acid solution until free from sulphuric acid. The precipitate and filter paper are then transferred into the second cylinder and titrated with $^N/_{10}$ alkali, using methyl orange as indicator, 0·1 c.c. $^N/_{10}$ NaOH being allowed for the picric acid used in washing, and the naphthalene content of the gas readily calculated from the titration results.

---

[1] *J. Gas Lighting*, 1900, **76**, 114.

[2] *J. Gasbeleuchtung*, 1916, **49**, 525-530, 540-543; *Gas Journal*, 1917, **137**, 64-69.

Jorissen and Rutten[1] point out that low results are obtained by the original Colman-Smith method if the precipitate of naphthalene picrate is washed with much water. They find, moreover, that when precipitated from a saturated solution of picric acid containing also solid picric acid, the naphthalene picrate is undissociated. Their procedure is as follows: A volume of 250 c.c. of a cold saturated solution of picric acid in water is evaporated down to 150 c.c., and while hot is transferred to two wash bottles. The gas is freed from tar-fog, cyanogen, hydrogen sulphide and ammonia, and is then passed through the bottles at a rate of about 1·5 cub. ft. per hour until a fair amount of precipitate is produced in the first bottle. The solution and precipitate are then washed into a flask, the volume made up to 250 c.c., the flask closed and heated to 40° C. for about half an hour and shaken until all the picrate has dissolved. After cooling, the solution is filtered and an aliquot part of the filtrate titrated with $^N/_{10}$ alkali, the titration value of the original solution being likewise determined.

For general gas works purposes a satisfactory method is to absorb the naphthalene in an alcoholic solution of picric acid made up by adding one volume of alcohol to four volumes of saturated aqueous solution of picric acid.[2] In this case no dissociation of naphthalene picrate occurs and the process of heating *in vacuo* adopted by Colman and Smith may be omitted.

Gair[3] employs acetic acid (sp. gr. 1·044) as an absorbent, a procedure which appears to possess advantages when working with gas at a temperature much higher than that of the atmosphere. Napthalene is precipitated as usual from the solution by the addition of picric acid solution and may be determined volumetrically or gravimetrically.

MICRO-GAS ANALYSIS. THE DETERMINATION OF SMALL PERCENTAGES OF VARIOUS CONSTITUENTS IN GASEOUS MIXTURES.

The presence of a definite gas in a state of great dilution in a gaseous mixture has frequently to be qualitatively determined. When present, the quantitative determination of its amount may be of importance. It is proposed in the present section to describe briefly the methods available for the qualitative and quantitative determination of some such constituents.

---

[1] *J. S. C. I.*, 1909, **28**, 1179.

[2] Cf. Somerville, *ibid.*, 1907, **26**, 1263.

[3] *Ibid.*, 1905, **24**, 1279, and 1907, **26**, 1263.

Carbon Monoxide.—The determination of minute quantities of carbon monoxide is sometimes of extreme importance. Methods of different sensitivities are available. A method dependent upon the reducing action of carbon monoxide upon an ammoniacal solution of silver oxide has been used by Berthelot[1] and Dejust.[2] Merwet[3] has shown that 0·02 per cent. of carbon monoxide is detectable by the decoloration produced when the gas is passed into a solution containing silver nitrate and potassium permanganate acidified with nitric acid. Spitta[4] has devised a method whereby 1 part of carbon monoxide in 37,000 may be detected. The method depends upon the oxidation of the gas by passage with air or oxygen over heated palladium, the temperature being maintained between 150° C. and 160° C. The carbon dioxide produced is determined by absorption with standard baryta solution and titration with standardized oxalic acid solution. The flame test is recommended by Clowes[5] for the rapid and accurate detection of carbon monoxide in air. The height of the flame-cap increases proportionately to the percentage of carbon monoxide present in the air, but the value of the test is depreciated by the fact that the height of the flame-cap is influenced by other inflammable gases.

Methods dependent upon the reducing action of carbon monoxide on palladium chloride have been devised. Palladium chloride is reduced by carbon monoxide with the formation of metallic palladium.

$$PdCl_2 + CO + H_2O = Pd + 2HCl + CO_2.$$

It must be remembered that a similar reduction is produced by acetylene and other hydrocarbons. Winkler[6] has suggested that the depth of colour of the black cloud of reduced palladium produced when carbon monoxide is passed into a solution containing cuprous chloride and palladium chloride will serve for the determination of the amount of carbon monoxide present in the gas. The depth of colour can be readily measured by any of the usual forms of colorimeter or nephelometer, the comparison tube being filled with the solution in which the depth of colour is due to a known amount of carbon monoxide. Potain and Drouin[7] similarly used a solution of palladium chloride. The palladium chloride can be employed in the form of test papers. These are produced by soaking strips of filter paper in an aqueous solution of palladium chloride containing 0·02 gm. of the chloride in 10 c.c. The papers are dried and when required for use are moistened and suspended in a vessel containing a little water and 10 litres of the gas to be examined. The time required for the production of a black film in the paper is dependent upon the percentage of carbon monoxide present in the gas. If carbon monoxide is present to the extent of 0·05 per cent., the brilliant black film is obtained in a few minutes. A similar result is obtained in two hours if carbon monoxide is present to the extent of 0·01 per cent. Sulphuretted hydrogen, ammonia and reducing gases such as acetylene must be removed before the test is carried out. Fodor recommends that the carbon monoxide be first of all absorbed with blood, being afterwards expelled by heating the blood to 100° C. A slow current of air is aspirated through the blood and carries with it the carbon monoxide content of the blood. The air and carbon monoxide pass through a train of wash bottles containing respectively sulphuric acid, lead acetate, and palladium chloride. Gases such as ammonia and hydrogen sulphide are retained in the first and second wash bottles respectively, and the carbon monoxide reduces the palladium chloride in the last bottle or bottles of the train. The amount of reduction is determined colorimetrically as above The sensitiveness of the method is, according to Klepzoff, considerably increased if filter paper soaked in palladium chloride is used in place of the solution. A similar method employing a dilute solution of gold chloride has been used by Donau.[1] The gold chloride solution is initially very pale yellow, after reduction the colour is ruby red. Levy[2] has criticized the method and has shown that 0·5 per cent. of carbon monoxide is readily detectable. He points out that the method requires the prior removal of acetylene and hydrogen sulphide.

---

[1] *Compt. rend.*, 1891, **112**, 597.

[2] *Ibid.*, 1905, **140**, 1250.

[3] *Ibid.*, 1897, **124**, 621.

[4] *Arch. f. Hygiene*, **46**, 284-310.

[5] *British Association Report*, 1896.

[6] *Z. anal. Chem.*, 1889, **28**, 269.

[7] *Compt. rend.*, **126**, 938.

The Blood Test for Carbon Monoxide.—Carbon monoxide is readily detected both spectroscopically and colorimetrically by means of blood. The method depends upon the fact that the gas is readily absorbed by blood, with the formation of carboxyhaemoglobin, the oxygen of the oxyhaemoglobin being displaced by carbon monoxide.

Haldane[3] states that the colorimetric test is much more delicate and more suitable for quantitative estimations than the spectroscopic or any other known method of examining small samples of blood for carbon monoxide.

The Colorimetric Test.—This test was devised by Haldane.[4] A dilute solution of normal blood is first prepared by pricking the finger and shaking up a drop of blood so obtained with water until the resulting solution has a yellow tinge. Portions of the solution are placed in two test-tubes of equal diameter. Ordinary lighting gas is then passed into the solution in one of the tubes until the hæmoglobin is entirely saturated with carbon monoxide. The colour of the solution is then pink. A mouse is then introduced into the air to be tested and a drop of its blood, obtained by opening the heart, is introduced into a third test tube. The blood is diluted with water until the depth of tint is the same as that of the two other solutions. Comparing the tints of the solutions in the three tubes, it is possible to estimate, according as the mouse's blood solution approximates in tint to the one or the other of the two first solutions, to what extent the mouse's hæmoglobin was saturated with carbon monoxide. Two-thirds saturation of the mouse's blood with carbon monoxide corresponds with 0·16 per cent. of carbon monoxide in the air. Half saturation of the mouse's blood with carbon monoxide corresponds with 0·08 per cent. of carbon monoxide in the air, one-third saturation with 0·04 per cent. of carbon monoxide, one-fifth saturation with 0·02 per cent. of carbon dioxide. The test is carried out in daylight but in its absence, a lamp or incandescent gas burner with a blue glass chimney and opal globe may be used, or blue glass spectacles can be employed. The test can be carried out thus if a mouse is not available: The sample of air is collected in a bottle of about 100 c.c. capacity and the cork removed under a solution of normal blood in distilled water of strength about $\frac{1}{2}$ per cent. About 5 c.c. of the air in the bottle is allowed to bubble out and a similar volume of solution to enter. The cork is replaced and the bottle and the contents shaken for about ten minutes, light being carefully excluded from the bottle by covering with a cloth. The solution is then poured into a test tube and the percentage saturation of the hæmoglobin with carbon monoxide estimated as above described. The percentage of carbon monoxide (p) present is calculated from the percentage saturation S by the formula –

---

[1] *Akad. Wiss. Wien. Sitz.*, **114**, 79-84.
[2] *J. S. C. I.*, 1911, **30**, 1437.
[3] *The Investigation of Mine Air*, p. 148.
[4] *Methods of Air Analysis*, 1918, pp. 113-128.

$$p = \frac{0\cdot07\,S}{100 - S}.$$

If the oxygen percentage of the air be much diminished, a correction is necessary to the formula. If, for instance, it be reduced by one half, the calculated value of p is to be halved in order that the correct percentage of carbon monoxide may be obtained. Haldane[1] has devised a more exact colorimetric test in which the procedure is briefly indicated. A 1 per cent. solution of blood saturated with carbon monoxide is prepared, likewise a 1 per cent. solution of normal blood. A standard solution of carmine is then run into the solution of normal blood until the two solutions are matched colorimetrically. A colorimetric test has been devised by Kunkel and Wetzel in which reagents such as 15 c.c. of a 1 per cent. tannin solution, or 5 c.c. of a 20 per cent solution of potassium ferrocyanide are added to 10 c.c. of a normal 20 per cent. solution of blood and a similar volume of a 20 per cent. solution of blood containing carbon monoxide. Coagulation of the blood occurs, the precipitate in the normal blood being greyish-brown and that in the blood containing carbon monoxide reddish-brown. A comparison of the colours enables the amount of carbon monoxide present in the gas to be determined.

The Spectroscopic Test.—Oxyhæmoglobin (normal blood) possesses two absorption bands in the yellow and green, between Fraunhofer lines D and E. In the case of blood containing carboxyhæmoglobin, the bands lie close together and their borders are less sharp than is the case with normal blood. The difference in the respective sets of bands is accentuated by treatment of the solution of blood with reducing agents. Ammonium sulphide or ferrous ammonium tartrate is used in this connection. Vogel[2] recommends the following procedure: 100 c.c. of fresh blood are diluted with 50 c.c. of water and poured into a flask of about 6 to 10 litres capacity containing the air to be examined. The bottle is closed and shaken for about half an hour. Ten drops of the normal unaltered solution of blood and of that shaken up in the bottle *are now diluted to 20 c.c. and examined spectroscopically.* A few drops *of the reducing agent—ammonium sulphide or ferrous ammonium tartrate*—are added to each. Oxyhæmoglobin is thereby reduced to hæmoglobin, while carboxyhæmoglobin remains comparatively unaltered. The hæmoglobin formed yields one ill-defined absorption band between the two absorption bands of any unaltered oxyhæmoglobin, and the band extends beyond the limit of the latter two bands but not so far as the D and E lines. The bands with carboxyhæmoglobin remain practically unaltered. The relative intensities of the bands due to carboxyhæmoglobin and to reduced hæmoglobin are measured, the former being more or less obscured by the superimposed band of the latter, and therefrom it is possible to determine with some degree of accuracy the degree of saturation of the blood with carbon monoxide.[1]

---

[1] *Journal of Physiology*, 1897, **22**, 478, 233; Clowes and Redwood, *The Detection and Estimation of Inflammable Gas and Vapour in the Air*, p. 139. Haldane, *Methods of Air Analysis*, 1918, p. 119 *et seq.*

[2] *Ber.*, 1877, **10**, 792; 1878, **11**, 235.

Determination of Carbon Monoxide by Means of Iodine Pentoxide.—This method was employed by Gautier[2] for the accurate determination of traces of carbon monoxide in air; the method was introduced independently by Nicloux.[3] The reaction occurring is represented by the equation:—

$$5CO + I_2O_5 = 5CO_2 + I_2.$$

The quantitative determination may then be made either by determining the iodine liberated or by determination of the carbon dioxide formed. Nicloux advises passing the gas through a **U**-tube containing small pieces of potassium hydroxide, then over pumice soaked in sulphuric acid and lastly through a **U**-tube containing iodine pentoxide immersed in an oil bath at 150° C. An absorption tube containing 10 c.c. of sodium hydrate is placed after the tube containing iodine pentoxide. The air is aspirated through the train of tubes at a rate of about 10 c.c. per minute, or less. The sodium hydroxide absorbs the iodine vapour and this is afterwards liberated by the addition of a little sodium nitrate and a little sulphuric acid and extracted with carbon bisulphide or chloroform. The coloration obtained is compared with that given by a solution of potassium iodide containing 0·1 mg. per c.c. when treated in like manner with sodium nitrate and sulphuric acid and extracted with chloroform. The liberated iodine can also be very accurately determined by titration with $^{N}/_{100}$ sodium thiosulphate solution.[4] The carbon dioxide liberated can be determined by titration of the sodium hydrate solution with baryta solution. Gautier points out that traces of ethylene and acetylene diminish the oxidation of carbon monoxide. Levy[5] has found that this inhibitory effect is not exhibited if the oxidation is carried out at 170° C., and he suggests that the inhibition is due to the water produced by the oxidation of the ethylene, etc., and is prevented by employing a temperature above the point of dehydration of iodic acid. The method has been discussed in detail by Spitta.[6] A portable form of apparatus capable of giving results correct to 0·005 per cent. has been described by Graham.[1] In this the liberated iodine is absorbed in a solution of potassium or sodium iodide and titrated with a standard solution of sodium thiosulphate.

---

[1] See *Uffelmann*, *Arch. f. Hygiene*, 1884, **2**, 207.

[2] *Compt. Rend.*, 1898, **126**, 793, 931.

[3] *Ibid.*, 746.

[4] Kinnicutt and Sanford, *J. A. C. S.*, 1900, **22**, 14.

[5] *J. S. C. I.*, 1911, **30**, 1437.

[6] Spitta, *Arch. f. Hygiene*, **46**, 284.

Rideal and Taylor[2] have designed an instrument whereby the percentage of carbon monoxide in a stream of gas is recorded. The carbon monoxide is catalytically and preferentially oxidized to carbon dioxide, and this is subsequently absorbed by a stream of standard lime water. The conductivity of the solution is measured and automatically recorded and serves to record the percentage of carbon monoxide in the gas. The instrument is designed principally for the determination of the purity of the hydrogen used in ammonia synthesis.

Sulphur Dioxide.—Very small quantities of sulphur dioxide can be determined by absorption in iodine as already described. Haldane employs $^N/_{100}$ iodine solution and titrates the excess with $^N/_{100}$ sodium arsenite solution.

Bailey[3] has designed an apparatus for the determination of the sulphur dioxide in the atmosphere. In this the SO_2 is oxidized by the passage of the air up a tower packed with glass spheres, over which trickles a solution of hydrogen peroxide, the strength of which is such that it contains 1 mgm. of active oxygen per c.c.

The percentage of SO_2 present is then determined by precipitation of the resulting sulphuric acid as barium sulphate.

Hydrogen Sulphide.—According to Haldane[4] the frequently quoted statement that a man can breathe 1 or even 3 per cent of H_2S for a short time without injury is quite erroneous. Lehmann[5] found that air containing about 0·07 per cent. is just sufficient to cause death after exposure for about one hour in the case of various animals and of man. According to Haldane, hydrogen sulphide in very great dilution is readily recognized by its characteristic smell. This test is less distinctive when the proportion of hydrogen sulphide present exceeds 0·01 per cent., but then irritation of the eyes begins to be produced. In great dilution it may also be readily detected by its blackening action on filter paper moistened with a solution of acetate of lead. Well prepared "lead-paper" is an extremely delicate agent for the detection of minute traces of hydrogen sulphide. The most satisfactory test papers may be prepared by moistening sheets of filter paper with a solution of 1 part of sugar of lead in 8 or 9 parts of water and holding each sheet while still damp over the surface of a strong solution of ammonia for a few minutes. The ammonia escapes as the test paper dries. When such papers are immersed, for say half an hour, in a large volume of gas, very minute traces of sulphuretted hydrogen will give a brown stain. Light should be excluded from the gas during the test. It is often convenient that the gas issue from a small orifice and impinge directly upon the paper. The delicacy of the test is increased by using a moist test paper. Various attempts have been made to determine a scale whereby the percentage of hydrogen sulphide present may be ascertained from the colour imparted to the test paper after passage of a determined volume of gas. It is doubtful, however, whether such scales afford any true indication of the percentage of hydrogen sulphide in the gas. When a paper is exposed to a slow stream of gas after the manner prescribed by the Gas Referees, 1 part of hydrogen sulphide per 1,000,000 is readily detected in 3 minutes. According to Lehmann, after passage of 8 litres of air at the rate of 12 litres per hour through a tube 12 mm. in diameter, a pale brown colour is formed when hydrogen sulphide is present to the extent of from 0·0001 per cent. to 0·0002 per cent., the paper being held at the outlet of the tube. A strong yellowish brown colour is obtained when the percentage present is 0·0003 per cent., while 0·0005 per cent. gives a dark brown colour and 0·0008 per cent. a brownish black colour. When making comparative tests of this nature, attention should always be paid to the method of impingement of the gas upon the paper. Butterfield[1] states: "The two sides of a piece of lead acetate paper $\frac{1}{2}$ sq. in. in area become something approaching light oak colour when brought in contact with 0·007 c.c. of H_2S". Wright[2] has described a method for the determination of the hydrogen sulphide contained in coal gas, which is essentially a modification of a method originally due to Fresenius. The hydrogen sulphide is absorbed by cuprous phosphate contained in a U-tube.

---

[1] *J. S. C. I.*, 1919, **38**, 10T.

[2] *Analyst*, 1919, **44**, 89-94.

[3] *The Atmosphere of Manchester. Report to the Manchester Field Naturalists' Society*, 1891.

[4] *The Investigation of Mine Air*, Foster and Haldane, 1905, p. 149.

[5] *Arch. f. Hygiene*, 1892, **14**, 135.

Hydrogen Phosphide.—The determination of traces of this gas in technical acetylene is of great importance. A qualitative test for harmful impurities is to allow the acetylene to impinge upon a black filter paper soaked with mercuric chloride and moistened with 10 per cent. hydrochloric acid. The presence of phosphorus, sulphur or silicon compounds is indicated by a white stain. A variation of this test is to bubble the gas through an acid solution of mercuric chloride.

For the quantitative determination, hydrogen phosphide is oxidized to phosphoric acid. Lunge and Cedercreutz[3] use sodium hypochlorite for this purpose and precipitate the phosphoric acid with magnesia mixture. There is risk of explosion when passing the acetylene through a solution of sodium hypochlorite.

Eitner and Keppeler[4] burn the acetylene in a special burner giving a non-luminous flame, and aspirate the products of combustion through a glass hood and through bulbs containing water and sodium hypobromite solution. The phosphoric anhydride deposited in the glass hood is washed out with water containing a little hydrochloric acid. The washings are evaporated with ammonium carbonate, redissolved and filtered to remove silica. The filtrate is then mixed with the solutions in the bulbs and phosphoric acid precipitated with ammonium molybdate. Gatehouse[5] burns the gas at the rate of 10 litres per hour in an ordinary burner under a bell jar. The products of combustion leave the bell jar through a drying tower and a long condensing tube which acts as a chimney and down which a little water is allowed to trickle. At the conclusion of the test the apparatus is allowed to cool and washed out with water. The phosphoric acid in the condensate and washings is titrated with N/10 caustic soda solution, using phenolphthalein as indicator. Further details of these determinations will be found in Lunge and Keane's *Technical Methods of Analysis*, Vol. 2, or in Leeds and Butterfield's *Acetylene*, 1910.

---

[1] *Chemistry in Gas Works*, 1913, p. 56.

[2] *J. C. S.*, 1883, **43**, 267.

[3] *Z. ang. Chem.*, 1897, **10**, 651.

[4] *J. Gasbeleucht*, 1901, **44**, 548.

[5] *Acetylene*, 1908, **5**, 167; 1909, **6**, 58.

Ammonia.—Traces of ammonia may be readily detected by means of either turmeric or hæmatoxylin paper, or paper saturated with Nessler's solutions. Turmeric paper is prepared by impregnating bibulous paper with an alcoholic solution of turmeric. The colour of the paper is turned reddish-brown by ammonia, but is bleached if hydrogen sulphide be present. Hæmatoxylin paper is prepared as follows.[1] Bibulous paper is washed with dilute HCl, then rinsed thoroughly with distilled water. The paper is immersed in a solution prepared by digesting 10 parts of logwood for several hours with 40 parts of alcohol and 120 parts of water. The liquid is heated with 0·7 part of alum (free from iron) a[illegible]·7 part of calcium chloride dissolved in the smallest possible amount of water acidified with HCl, which is added drop by drop until a red coloration sufficient to tint the paper is obtained. When dry, the paper is slightly yellow or pink. It becomes blue in the presence of alkalies and is extremely sensitive to ammonia.

Nessler's solution is prepared in the manner already described under Water Analysis. For the exact determination of a minute trace of ammonia present in air or other gas, a definite volume of the gas is passed into water slightly acidified with sulphuric acid, the absorbed ammonia being subsequently determined colorimetrically. A solution of Rochelle salt prepared as follows is required: Fifty grams of Rochelle salt are dissolved in 100 c.c. of hot water; 5 c.c. of Nessler's solution are added to prevent the formation of mould and the solution kept in the dark. When necessary the Nessler solution and the solution of Rochelle salt may be filtered through a plug of cotton wool. The ammonia determination is then carried out in the following manner[2]: 100 c.c. of the solution containing ammonia absorbed by sulphuric acid is placed in a glass stoppered vessel of about 150 c.c. capacity. A similar volume of water free from ammonia is placed in a second similar glass vessel. 2 or 3 c.c. of the Rochelle salt solution prepared as above are added to the contents of each vessel, followed by the same amount of Nessler's solution added drop by drop with stirring. To the contents of the vessel containing the ammonia-free water, a standard solution of ammonium chloride (1 c.c. = 0·1 mg. NH_3) is added drop by drop until, after shaking, equality of colour is obtained in the case of the contents of both glass vessels. Permanent colour standards for the comparison may be prepared from solutions of platinum and cobalt salts as recommended by the American Committee on Water Analysis, 1905.

Special Physical Methods.—Special methods utilizing the difference in thermal, optical, and electrical properties of various gases have been devised for the determination of small percentages of gases in gaseous mixtures. The delicacy of the optical method utilizing the spectra of the various gases is extreme, the electric discharge in an exhausted tube containing a trace of a gaseous mixture, enabling one to detect with certainty and in some cases to determine quantitatively the minutest trace of a gaseous constituent. This optical method is most highly developed in the case of the rare gases—helium, argon, neon, etc., and the reader is referred to books such as Baly's *Spectroscopy* (Longmans) and Travers' *Study of Gases* (Macmillan) for details of technique. The methods depending upon the thermal and electrical properties of the gases and of their solutions, being strictly physical in character, hardly fall within the scope of this work. Mention may be made of Shakespear's[1] hydrogen-purity meter or katharometer. In this, two platinum wires are immersed in chambers containing gas, the one gas pure hydrogen and the other hydrogen together with some impurity. The two wires form arms of a Wheatstone bridge through which a pre-determined distribution of current is maintained and balance of the bridge is obtained when both samples of gas are pure hydrogen. The balance of the bridge is upset owing to the diminished thermal conductivity of the gaseous medium containing a gas other than hydrogen. The deflection of the pointer of the galvanometer indicates the percentage of hydrogen present. The method is one of wide application but is of extreme sensitiveness in the case of hydrogen owing to the unique high thermal conductivity of that gas. Mention may also be made of the electrical method devised by Campbell[2] using the Pirani pressure gauge.

---

[1] *Reagents and Reactions*, Tognoli, translated by C. A. Mitchell, 1918, p. 195.

[2] *Chem. Zeit.*, 1899, **23**, 454 and 511; 1901, **25**, 586.

THE MEASUREMENT OF GASES EVOLVED FROM LIQUIDS AND SOLIDS.

Methods of analysis depending upon the measurement of the volume of gas evolved by a reaction were rendered more easily applicable and more accurate by the introduction of Lunge's apparatus. This was originally devised for the determination of nitrogen acids in vitriol in connection with the control of chamber acid plants, and hence is generally known as a nitrometer, but with modification it may be adapted for a variety of purposes, e.g. in conjunction with Hempel and other similar pipettes. The simplest form of nitrometer is shown in fig. 173 and consists of a graduated measuring tube *a* to the top of which is fused a three-way stop-cock carrying a glass cup as shown. The graduations on *a* extend from the top downwards and in this type the total volume may be 50 c.c. divided into $^1/_{10}$ c.c. The reservoir or pressure tube *b* is ungraduated and is about the same size as the burette, to which it is connected by means of a suitably protected pressure tube. Both tubes are held in clamps on an iron stand, and the ready removal and replacement of the measuring burette are facilitated by the provision of a strong spring clamp. The apparatus is very suitable for the use of mercury so that gases soluble in water may be measured.

In the analysis of substances (e.g. solid nitrates) where it is desired to measure a larger volume of gas than 50 c.c. the capacity of the measuring burette is increased by blowing a bulb (of say 100 c.c. capacity) just below the tap (see fig. 114). In this case a similar bulb is blown at the bottom of the pressure tube to contain the extra displaced mercury.

---

[1] See *Proc. Roy. Soc.*, 1920, 685A, 273.

[2] *Proc. Phys. Soc.*, 1920-21, **33**, 287.

The apparatus is manipulated as follows: the burette is filled with mercury and all air expelled from the burette and the two bore holes of the tap, a small mercury seal being left in the cup. If the gas to be measured is generated in some external vessel, that vessel is connected to the side limb of the tap and the gas volume is easily measured at atmospheric temperature and pressure.

In cases, such as the determination of nitrogen acids in vitriol, where the gas is generated within the burette, the liquids are introduced to the burette through the cup. The liquid having been poured on to the surface of the mercury in the cup, the tap is cautiously opened and closed just when all the liquid has run into the burette. If any air is introduced at this stage it must be at once expelled by raising the pressure tube. The reagent (pure sulphuric acid in the case cited) is next introduced in the same way and this serves to rinse the sample out of the cup. The burette is taken from the clamp and cautiously shaken until the reaction is complete, and is then allowed to stand until all froth has subsided and until the gas has assumed atmospheric temperature. In reading the gas volume allowance is made for the head of liquid in the burette by so placing the tubes that the mercury in *b* is as much higher than that in *a* as is required to balance the liquid in *a*. The relative specific gravity of mercury and liquid must be known for this purpose. If this adjustment has been correctly made the mercury level should not be affected by opening the tap to the atmosphere.

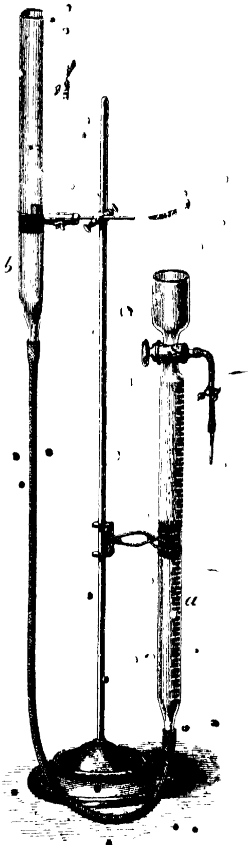

FIG. 113.

Other modifications introduced by Lunge[1] are shown in figs. 115 and 116. These figs. show the Greiner and Friedrich tap, which is much to be preferred when making connections with other apparatus. The cup is eliminated from the types shown in figs. 114 and 116 as this is not required except for the introduction of liquids. These illustrations show the flask with an inner tube fused on to its bottom. This flask is used in the analysis of permanganates, chloride

[1] *J. S. C. I.*, 1890, 9, 21.

of lime, manganese dioxide, etc., and is suspended from the tap of the nitrometer as shown. The nitrometers used for such gas volumetric analyses are best graduated in such manner that the zero point is about a centimetre below the tap. The general manipulation is as follows: The mercury is adjusted to the zero mark, or to 1·0 c.c. in the case of nitrometers graduated from the tap itself (in which case, of course, 1·0 c.c. is deducted from all subsequent readings). After this adjustment the glass tap is closed. The substance to be tested and the reagent, if any, are placed in the flask and the connection made with the nitrometer as shown. The air within the flask will now be slightly compressed so that it is neces-

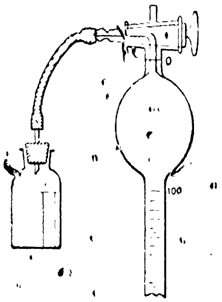

FIG. 114.

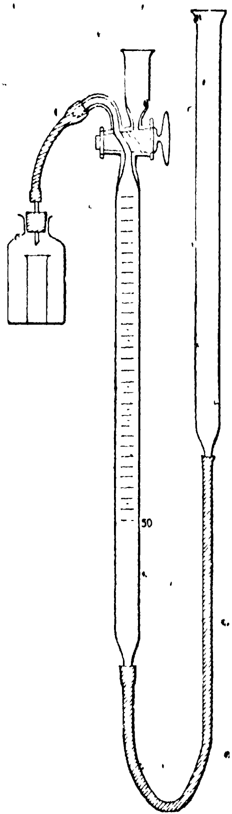

FIG. 115.

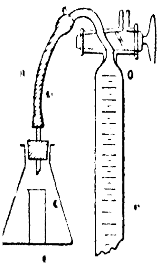

FIG. 116.

sary to make momentary connection with the atmosphere by turning the tap shown in fig. 114, or by removing the key of the Greiner and Friedrich tap.

The measuring burette is then placed in connection with the reaction flask, the liquids are mixed in the flask and as the reaction proceeds the gas is passed over into the burette. The pressure tube is adjusted during the reaction to maintain approximately atmospheric pressure within the flask. When the reaction is complete the volume of moist gas is read off at atmospheric temperature and pressure. Lunge and Schmidt[1] used two nitrometer vessels arranged as shown in figs. 117 and 118 for the collection and measurement of gases dissolved in water. The flask A is

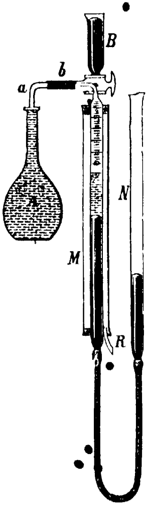

Fig. 117.

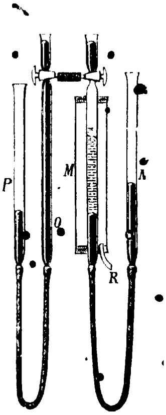

Fig. 118.

completely filled with water; an india-rubber plug with a capillary tube (*a*) passing through it is then inserted in the flask, and the tube is thereby completely filled with water. The whole is then weighed, and the difference between this and the weight of the empty flask and tube gives the amount of water taken. The end of the capillary tube is then connected to the side tube of the nitrometer by the tube *b*. The nitrometer is then completely filled with mercury, and, when the tubes are quiet, the flask and measuring tube of the nitrometer are quickly placed in connection without the introduction of the slighest trace of air. The water in the flask is then slowly heated to boiling. Some water as well as the dissolved gases collect in the measuring tube of the nitrometer. The tube N should be lowered in order that the boiling may take place under

---

Z. a. Chem., 1886 **25**, 309.

reduced pressure. After boiling for 5 to 10 minutes, the stop-cock is quickly turned through 180°, so that the flask is placed in communication with the cup B containing mercury, and the flame removed.

Since the mercury stands lower in N than in M, it is not possible for any loss of gas to take place at the moment of turning the tap. It is also impossible for any gas or steam to escape through the mercury cup, since the pressure is inward. A small bubble of gas always remains under the stopper; this is brought into M by lowering the tube N as much as possible, and then turning the stop-cock so that the flask and measuring tube are again placed in connection, and when the bubble has passed over, quickly reversing the tap again.

When the whole of the gas is collected in the nitrometer, it is connected with a second instrument, OP, quite full of mercury. The gas is then transferred by placing the tap in such a position that it is closed in all directions, and the tube M is heated by passing steam through the tube R. When it is quite hot the tube N is lowered, causing the water in M to boil, thus expelling every trace of dissolved gas. The taps are then placed in connection and the gas passes over. It can then be cooled, measured, and submitted to analysis.

The device introduced for the elimination of the calculations necessary to reduce the gas volume to normal temperature and pressure has already been explained (p. 524). This is incorporated in the apparatus shown in fig. 119. A is the measuring burette and B the compensating tube. E is an external reaction vessel which may be used in place of the reaction flask previously described. When using this vessel the capillary tube *a* is filled with mercury and whilst the vessel is being shaken this mercury is held in position by the rubber cap *b*. The vessel E is then operated just as an ordinary nitrometer, the liquids being introduced through the cup *c*. When the reaction is complete the gas is tranferred to A for measurement, connection being made between the two vessels by means of the rubber connection *d* after removal of the cap *b*. To effect the transference, the taps on E and A are turned, F is raised and C lowered until the liquid in E just reaches the tap on A.

It will be observed that with this form of apparatus the vessels A and B need not be removed during an analysis, they may, therefore be conveniently water-jacketed in order to facilitate the regulation of temperature.

In technical work, where the instrument is always used for the same purpose, a further saving in time is effected by so graduating the measuring burette, that when using a fixed quantity of substance, percentages may be read off directly. In some cases, when making such graduations it is necessary to make allowance for the incompleteness of the reaction; for instance in the hypobromite determination of urea only 91 per cent. of the nitrogen can be measured.

On some burettes the weight of a certain gas is marked alongside the volumetric graduation marks.

Japp[1] introduced a modified method of using the gas volumeter, by means of which, with ordinary 50 c.c. gas burettes A and B (fig. 120), any

---

[1] J. C. S., 1891, 59, 894.

[illegible] may be, measured under such conditions that each c.c. represents a milligram of the gas. The name "gravi-volumeter" is given to this instrument and it possesses the advantage over the specially graduated burettes described above that one instrument can be used for different substances. In using the instrument, that volume of air which 25 c.c. of dry air at N.T.P. would occupy when measured moist at atmospheric temperature and pressure is introduced into the regulator

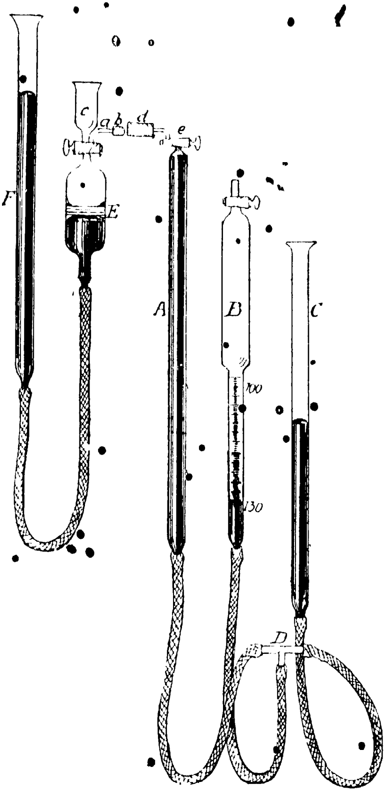

FIG. 119.

tube B. Calculation is then made, for any particular gas to be measured in A, of the volume to which 25 c.c. of the dry gas at N.T.P. must be brought so that 1 c.c. may correspond with 1 mgm. of the gas. For example, 25 c.c. dry nitrogen at N.T.P. weigh 0·0313 gm., thus the required volume is 31·3 c.c. This is termed the "gravi-volumetric value" for nitrogen and the division 31·3 on the tube B is permanently marked N_2.

Corresponding values are in like manner determined for other gases and marked on the tube; some values given by Japp are: methane 17·9, air 32·3 and carbon dioxide 49·4.

When it is desired to ascertain the weight of a given gas contained in the tube A, the reservoir C is adjusted so that the mercury in B stands at the gravi-volumetric value of the gas being measured; at the same time A and B are so placed that the mercury levels in those tubes are the same. In these circumstances each c.c. of gas in the tube A represents 1 mgm. Fig. 120 shows the position of the tubes when measuring off 20 mgm. of nitrogen; since in the tube B 25 c.c. of dry air at N.T.P. have been made to occupy 31·3 c.c., every 25 c.c. of dry nitrogen at N.T.P. in the tube A occupies 31·3 c.c., because the conditions as regards temperature, pressure, and saturation with aqueous vapour are the same in the two tubes. As shown above, 25 c.c. of dry nitrogen at N.T.P. weigh 31·3 mgm., so that an observed volume of 31·3 c.c. would represent 31·3 mgm., or the volume (20 c.c.) observed in this case represents 20 mgm. Lunge[1] prefers to use a larger volume than 25 c.c. of dry air as the basis of such an apparatus.

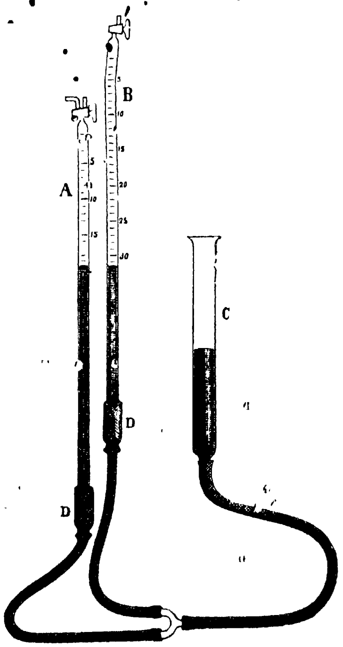

FIG. 120.

---

[1] *Ber.*, 1892, 25, 3162.

Planchon[1] describes a manonitrometer which he introduced for the analysis of nitrates, etc., in order to overcome errors due (1) to the small amount of substance taken in an ordinary nitrometer determination, and (2) to the air always contained in a sulphuric acid solution of nitrate. The apparatus consists of a flask fitted with a three-way tap which gives connection with the atmosphere and/or with a barometer tube dipping into mercury and furnished with a movable scale. A known weight of the substance (say 2·5 gm. nitrocotton or 5 gm. of nitrating acid) and fixed volumes of sulphuric acid and mercury are placed in the flask, which is then exhausted by a water pump. The scale is adjusted so that the mercury in the barometer tube stands at zero, and the flask is then shaken violently until the evolution of gas is complete, as indicated by a constant reading on the barometer tube. The temperature is noted by immersing the flask in water, and the volume of gas evolved is calculated from the observed temperature and pressure and the known capacity of the flask and barometer tube.

The following are some of the commoner analyses which are carried out in the forms of apparatus just described :—

1. Determination of Nitrogen Acids.—It was for the analysis of nitrous vitriol, etc., that the original Lunge nitrometer was designed. This determination is based upon the following reactions with mercury and sulphuric acid :—

$$2HNO_2 + 2Hg + H_2SO_4 = 2H_2O + Hg_2SO_4 + 2NO$$
$$2HNO_3 + 6Hg + 3H_2SO_4 = 4H_2O + 3Hg_2SO_4 + 2NO.$$

According to the strength of the nitrous vitriol, 0·5 to 5·0 c.c. are taken with about 6 c.c. of pure concentrated sulphuric acid. The nitrometer must be well shaken to ensure reaction with the mercury. All the nitrogen in the nitrogen acids is evolved and measured as nitric oxide.

The process is readily applicable to the analysis of nitrates, nitroglycerol, nitrocellulose, etc., such a weight of substance being taken in concentrated solution as will give a volume of nitric oxide appropriate to the nitrometer in use. Each c.c. of NO measured at 0° C. and 760 mm. pressure dry weighs 1·3402 mgm.

The equivalent weight of	N_2	is	0·626	mgm.
,,	,, N_2O_3	,,	1·698	,,
,,	,, N_2O_5	,,	2·412	,,
,,	,, HNO_3	,,	2·814	,,
,,	,, $NaNO_3$	,,	3·799	,,
,,	,, KNO_3	,,	4·516	,,

2. Nitrogen.—The apparatus may be used for the measurement of nitrogen in the analysis of organic substances by Dumas' method. Each c.c. of nitrogen measured at 0° C. and 760 mm. pressure dry weighs 1·2507 mgm.

3. **Ammonia Salts.**—For the determination of ammonia by the hypobromite method, the reaction flask shown in fig. 115 is employed. About 0·25 gm. of the solid substance (or an equivalent of solution) is placed in the flask and about 10 c.c. of sodium hypobromite solution are placed in

---

[1] *Ann. Chim. Analyt.*, 1915, **20**, 189.

the inner tube. The hypobromite solution is freshly prepared by dissolving 2·5 c.c. of bromine in 25 c.c. of 30 per cent. NaOH solution. The flask is gently shaken to complete the evolution of nitrogen; it is found in practice that only 97·5 per cent. of the nitrogen is evolved so that for purposes of calculation each c.c. of nitrogen measured is taken as equivalent to 1·283 mgm. N_2 or 1·559 mgm. NH_3.

4. **Urea** is similarly determined, but in this case only 91·5 per cent. of the nitrogen is evolved. Allowing for this correction, each c.c. of nitrogen measured represents 2·929 mgm. urea.

5. **Carbonates** are determined by decomposition with acid in the reaction flask. Each c.c. of CO_2 measured at 0° C. and 760 mm. pressure dry represents 1·977 mgm. CO_2.

6. **Permanganates**, etc.—For the determination of available oxygen, an acid solution of permanganate is treated with excess of hydrogen peroxide in the reaction flask. Each c.c. of oxygen measured represents 0·7145 mgm. available oxygen in the permanganate. Manganese dioxide in ores may be similarly determined if the carbonates are first decomposed by dilute acid. Each c.c. of O_2 measured represents 3·882 mgm. MnO_2.

7. **Hydrogen Peroxide** may be determined by treatment with excess of acidified permanganate solution. Each c.c. of O_2 measured represents 1·520 mgm. H_2O_2.

8. **Bleaching Powder.**—The available chlorine in bleaching powder, etc., may be determined by reaction with hydrogen peroxide. Each c.c. of O_2 measured represents 3·167 mgm. available chlorine In order to avoid the confusion which has crept into certain text-books it should be noted that by "available chlorine" is meant the total Cl_2 contained in $Ca(OCl)Cl$, or the chlorine equivalent of the oxygen available for oxidation.[1]

---

[1] See *Chem. and Met. Engineering*, 1920, **23**, 1064.

	Solubility in Water.		
=1.	At 0° C.	At 15° C.	At 30° C.
	A 1·730	1·208	0·934
	A 1299	802	595/28° C.
	A 0·058	0·040	0·030
	—	—	—
	—	—	—
	—	—	—
	—	—	—
	A 1·713	1·019	0·665
	A 0·0354	0·0251	0·020
	—	S 2·635	1·769
	—	α 4·05	—
	A 0·098	0·058	0·040
	A 0·226	0·109	—
	A 0·0150	0·0139	0·0138
	—	A 425/10° C.	—
	S 612	565	517
	S 506·7	458·4	411·5
	—	—	—
0	A 0·0215	0·0190	0·0170
	A 4·686	3·056	2·21
	A 0·0556	0·0369	0·0276
3	A 0·074	0·051	0·040
7	A 0·0239	0·0179	0·0138
3	—	—	—
3	A 1·05/5° C.	0·74	0·63/20° C.
1	A 0·0489	0·0342	0·0261
	α 0·64	0·46	0·19/32° C.
	—	—	—
	—	A 0·065/18° C.	—
	α 0·446	0·379	—
	S 79·8	47·3	27·2
	A 0·0294	0·0205	0·0157

veight of gas + weight of water vapour) contained
C. and a total pressure 760 mm. are to be calculated

the *total* pressure of the gas is 760 mm. of mercury,

e following significance Winkler draws a distinc-
lume of the gas (reduced to 0° C. and 760 mm.) which
ır pressure of water) is 760 mm. The coefficient of
er) when the pressure of the gas *itself* is 760 mm
value when the solvent evaporates into an otherwise

m. by the gas contained in unit volume *of the solution*.
ecified.

[*To face p.* 598.

INDEX TO PART IX.

THE VOLUMETRIC ANALYSIS OF GAS.

Absorption, determination by, 530, 534, 549, 550.
Acetylene, calorific value of, 573.
— determination of, 530, 534, 539, 543.
— hydrogen phosphide in, 588.
— physical characteristics of, *facing* 599.
Air, physical characteristics of, 528.
Alkali, etc., Works Regulation Act, 574.
Ammonia, determination of, 530, 534, 576, 589, 597.
— physical characteristics of, *facing* 599.
Apparatus used for gas analysis, 550-572.
Argon, determination of, 590.
— physical characteristics of, 599.
Arndt (and Knorre), 577.
Aspirator, Fletcher's, 574.
Aston, determination of oxygen, 533

Bailey, determination of sulphur dioxide, 587.
Balcon, determination of nitrogen, 546.
Bedson, apparatus, 571.
Benzene, calorific value of, 573.
— determination of, 530, 534, 539, 543, 578, 580.
— physical characteristics of, *facing* 599.
Berthelot, determination of carbon monoxide, 583.
Bone and Jerdan, determination of hydrogen, 550.
— and Wheeler, apparatus, 546, 554.
Boyle, law of gases, 521.
Bunsen, absorption tube, 510.
— coefficients of absorption, *facing* 599.
— determination of hydrochloric acid, 532.
— electrolytic gas, 538.
— eudiometer, 510.
— meniscus correction, 5[illegible]8.
Bunte, combustion over palladium, 547.
Burettes, calibration of, 515-520.
— gas, 510-520.
— graduation of, 512-515.
Burgess and Wheeler, determination of paraffins, 541.
Burrell and Seibert, relative densities of gases, 539.
— Seibert and Robertson, determination of vapours, 580.
Butane, determination of, 537, 539.
— physical characteristics of, *facing* 599.
Butterfield, determination of hydrogen sulphide, 588.
Butylene, determination of, 5[illegible]
— physical characteristics of, *facing* 599.

Caldwell (and Macfarlane), 558.
Calorific values of gases, 572.
Campbell, determination of vapours, 580.
Carbon bisulphide, determination of, 578.
— — physical characteristics of, *facing* 599.
— dioxide, determination of, 531, 534, 598.
— — physical characteristics of, *facing* 599.
— monoxide, calorific value of, 573.
— — determination of, 531, 534, 537, 539, 542, 546, 583.
— — physical characteristics of, *facing* 599.
Carbonates, analysis of, 598.
Cathetometer, 510.
Cedercreutz (and Lunge), 588.
Charles, law of gases, 521.
Chloride of lime, analysis of, 591, 592.
Chlorine, determination of, 598.
— physical characteristics of, *facing* 599.
Clark, mercury still, [illegible]06.
Clowes, determination of carbon monoxide, 583.
— — — oxygen, 532.
Colman, determination of hydrocyanic acid, 578.
— and Smith, determination of naphthalene, 580.
Coquillion, grisoumeter, 565.
Cuprous chloride solution, preparation of, 531.
Cyanogen, determination of, 539.
— physical characteristics of, *facing* 599.

Damiens (and Lebeau), 580.
Davis, determination of vapours, 579.
— (and Taylor), 577.
Dejust, determination of carbon monoxide, 583.
Denham, fractional combustion, 546.
Dennis, absorption pipettes, 572.
— and M'Carthy, determination of benzene 530.

Density of gases, *facing* 599.
Deville, determination of benzol, 599.
Dittmar, apparatus, 558.
Donau, determination of carbon monoxide, [illegible].
Drehschmidt, determination of carbon monoxide, 531.
— platinum capillary tube, 547.
Drouin (and Potain), 583.

EDWARDS, correction of gas volumes, 526.
Eitner and Keppeler, determination of hydrogen phosphide, 588.
Electrolytic gas, 538.
Ethane, calorific value of, 573.
— determination of, 531, 534, 537, 539.
— physical characteristics of, *facing* 599.
Ethylene calorific value of, 573.
— determination of, 531, 534, 539, [illegible].
— physical characteristics of, *facing* 599
— *see* benzene, 530.
Eudiometric tubes, 510-520.
— — calibration of, 515-520.
— — gradvation of, 512-515.
— — preparation of, 510.
Evans, determination of nitrogen, 545.
Explosion analysis, 538.
Explosive mixtures, [illegible].

FLETCHER's aspirator, 574.
Fodor, determination of carbon monoxide, 584.
Fox, determination of oxides of nitrogen, 576.
Fractional combustion, 541-550.
Frankland and Ward, apparatus, 551
Franzen, determination of oxygen, 533.
Fresenius, determination of hydrogen sulphide, 588.
[illegible] (and Gremer), 509.

GAILLARD, determination of oxides of nitrogen, 577.
Gair, determination of naphthalene, 582.
Gas Referees, determination of hydrogen sulphide, 588.
— — — — sulphur compounds, 578.
Gas volumeter, 524, 594.
Gases evolved from liquids, etc., measurement of, 590-598.
Gatehouse, determination of hydrogen phosphide, 588.
Gautier, determination of carbon monoxide, [illegible]
Geppert, meniscus correction, 518.
Gockel, meniscus correction, 518.
Graduating table, 512.
Graduation of burettes, etc., 512-515.
Graham, determination of carbon monoxide, 587.
Gray, determination of benzol, 580.
— sampling of gas, 502, 503.
Greiner and Friedrich, stop-cocks, 509.
Grisoumeter, 565.

HABER, explosion analysis, 540.
Hæmatoxylin paper, preparation of, 589.
Haldane, apparatus, 527, 560.
— determination of carbon monoxide, 584.
— — — hydrogen sulphide, 587.
— — — sulphur dioxide, 587.
Haller, determination of sulphur dioxide, 576.
Harcourt, determination of carbon bisulphide, 578.
Hartmann (and Paal), 532.
Helium, determination of, 590.
— physical characteristics of, *facing* 599.
Hempel, absorption of hydrogen, 550.
— apparatus, 568.
— correction of gas volumes, 526.
— fractional combustion, 546.
Hulett and Minchin, distillation of mercury, 506.
Huntly, sampling of gas, 503.
Hydriodic acid, physical characteristics of, *facing* 599.
Hydrobromic acid, physical characteristics of, *facing* 599.
Hydrochloric acid, determination of, 532.
— — physical characteristics of, *facing* 599.
Hydrocyanic acid, determination of, 577.
— — physical characteristics of, *facing* 599.
Hydrogen, absorption of, 549, 550.
— calorific value of, 573.
— determination of, 531, 534, 537, 539, 542, 546, 549, 590.
— physical characteristics of, *facing* 599.
— preparation of, 535, 571.
Hydrogen peroxide, analysis of, 598.
— phosphide, determination of, 588.
— sulphide, determination of, 533, 534, 587.
— — physical characteristics of, 599.

JACKSON, lubricant, 509
Jaeger, determination of nitrogen, 544.
— fractional combustion, 543.
Japp, gas volumeter, 594.
Jerdan (and Bone), 550.
Jones and Meighan, determination of oxygen, 533.
Jorissen and Rutten, determination of naphthalene, 582

KALETA, pipette, 549.
Katharometer, 590.
Keppeler (and Eitner), 588.
Kew principle correction tube, 523.
Kinnicut and Sanford, determination of carbon monoxide, 586.
Klepzoff, determination of carbon monoxide, 584.
Knorre and Arndt, determination of nitric oxide, [illegible].

Knublauch, determination of hydrocyanic acid, 578.
— — — naphthalene, 581.
Kunkel, determination of carbon monoxide, 585.
Küster, determination of naphthalene, 580.

LEATHER, determination of naphthalene, 580.
Lebeau and Damiens, determination of vapours, 580.
Lehmann, determination of hydrogen sulphide, 587.
— — — sulphur dioxide, 576.
Lessing, determination of benzol, 579.
Levy, combustion analysis, 548, 549.
— correction of gas volumes, 526.
— determination of carbon monoxide, 584, 586.
Lumpricht, determination of benzene, 580.
Lubrication of taps, 509.
Lunge, apparatus, 524, 590.
— and Cedercreutz, determination of hydrogen phosphide, 588.
— and Schmidt, nitrometer, 593.

M'CARTHY (and Dennis), 530.
Macfarlane and Caldwell, apparatus, 558.
McLeod, apparatus, 551.
Manganese dioxide, analysis of, 592
Manonitrometer, 597.
Mauguin (and Terres), 542.
Meighan (and Jones), 533.
Meniscus correction, 518.
Mercury, distillation of, 506.
— filtration of, 505.
— meniscus of, 518.
— purification of, 505-507.
Merwet, determination of carbon monoxide, 583.
Methane, calorific value of, 573.
— determination of, 534, 537, 539, 542, 546.
— physical characteristics of, *facing* 599.
Metrogas apparatus, 545.
Meyer and Seubert, apparatus, 554.
Micro-gas analysis, 582-589.
Minchin (and Hulett), 506.
Molecular weights, *facing* 599.
Moser and Schmid, fractional combustion, 549.

NAPHTHALENE, determination of, 580.
Nauss, determination of hydrocyanic acid, 578.
Neon, determination of, 590.
Nicloux, determination of carbon monoxide, 586.
Nitric oxide, determination of, 532, 576, 577, 597.
— — physical characteristics of, *facing* 599.
Nitrogen, determination of, 541, 544, 597.
— physical characteristics of, *facing* 599.
Nitrogen peroxide, density of, 529.
— — determination of, 576, 597.
Nitrometers, 524, 591.
Nitrous oxide, determination of, 577.
— — physical characteristics of, *facing* [illegible].
Normal gas solutions, 574.

OLEFINES, determination of, *see* benzene, 530, 534.
— — *see* ethylene, 531.
— nature of, 511.
Orsat-Lunge apparatus, 564.
Ostwald, calibration of burettes, 515.
Oxygen, determination of, 532, 534, 598.
— physical characteristics of, *facing* 599.
— preparation of, 535, 536.
Ozone, physical characteristics of, *facing* 599.

PAAL and Hartmann, determination of hydrogen, 532.
Palladium, preparation of colloidal, 532.
Palladiumized asbestos, 547.
Paraffins, nature of, 511.
Pentane, determination of, 539.
— physical characteristics of, *facing* 528.
Permanganates, analysis of, 591.
Pfeiffer, determination of benzene, 580.
Phillips, fractional combustion, 546.
Physical characteristics of gases, 539, *facing* 599.
— methods of analysis, 589, 590
Pirani pressure gauge, 580.
Planchon, manonitrometer, 597.
Platinum wires, sealing in, 510
Pollak, determination of nitrous oxide, 577.
Potain and Drouin, determination of carbon monoxide, 583.
Propane, determination of, 537, 539, [illegible]
— physical characteristics of, *facing* 599.
Propylene, calorific value of, 573.
— determination of, 533, 539.
— *see* ethylene, 531.
— physical characteristics of, *facing* 599.
Pyrogallate solutions, preparation of, 532.

REGNAULT and Reiset, apparatus, 551.
Rhead, determination of benzol, 579.
— and Wheeler, reagents, 534.
Richardt, fractional combustion, 546, 547.
Rideal and Taylor, determination of carbon monoxide, 587.
Robertson (and Burrell), 580.
Russell, apparatus, 551.
— (and Williamson), 522, 551.
Rutten (and Jorissen), 582.

SAMPLING, methods of, 499-505.
Sanford (and Kinnicutt), 586.
Schmid (and Moser), 549.
Schmidt (and Lunge), 593.

eibert (and Burrell), 539, 580.
eubert (and Meyer), 554.
hakespeare, determination of hydrogen, 590.
ilver chloride solution, preparation of, 530.
Skirrow, determination of hydrocyanic acid, 578.
Smith, determination of nitrogen, 544, 546.
— (and Colman), 580.
Sodeau, apparatus, 523, 528, 565.
— determination of oxygen, 533.
— sampling of gas, 502.
Solubility of gases, 528, *facing* 599.
Somerville, determination of naphthalene, 532.
— — — sulphur compounds, 578.
Spitta, determination of carbon monoxide, 583, 586.
Stop-cocks, 507-509.
Sulphur compounds, determination of, 578.
— dioxide, determination of, 533, 576, 587.
— — deviation from Boyle's law, 574.
— — physical characteristics of, *facing* 599.

Taplay, combustion analysis, 544.
— determination of olefines, 531.
Taylor (and Rideal), 587.
— and Davis, determination of oxides of nitrogen, 577.
Terres and Mauguin, fractional combustion, 542.
Thiophen, determination of, 580.
Thomas, apparatus, 551.
— explosive mixtures, 537.
Titoff, determination of sulphur dioxide, 576.
Titration, determination of gases by, 573-582.
Travers, determination of oxygen, 533.

Uffelmann, determination of carbon monoxide, 586.
Urea, determination of, 598.

Van Alstine, absorption pipettes, 572.
Vapours, determination of, 579, 580.
Vogel, determination of carbon monoxide, 585.
Volumes, correction for temperature and pressure, 520-528.

Ward (and Frankland), 551.
Watson, determination of oxygen, 533.
Wetzel, determination of carbon monoxide, 585
Wheeler (and Bone), 546, 554.
— (and Burgess), 541.
— (and Rhead), 534.
Wibaut, combustion analysis, 514.
Williamson and Russel, apparatus, 551.
— — — correction of gas volumes, 522.
Winkler, coefficient of solubility, 528.
— correction of gas volumes, 522.
— -Dennis combustion pipette, 547.
— determination of carbon monoxide, 583.
— fractional combustion, 546, 547.
— meniscus correction, 518.
Wright, determination of hydrogen sulphide, 588.

APPENDIX OF TABLES.

TABLES.

TABLE I.

Pressure of Aqueous Vapour in Millimetres of Mercury, from − 9·9° to + 35° C.

°	mm.	°	mm.	°	mm.	°	mm.	°	mm.	°	mm.
−9·9	2·096	−5·4	3·031	−0·9	4·299	3·5	5·889	8·0	8·017	12·5	10·804
·8	·114	·3	·058	·8	·331	·6	·930	·1	·072	·6	·875
·7	·132	·2	·082	·7	·364	·7	·972	·2	·126	·7	·947
·6	·150	·1	·106	·6	·397	·8	6·014	·3	·181	·8	11·019
·5	·168	−5·0	·131	·5	·430	3·9	·055	·4	·236	12·9	·090
−9·4	·186	−4·9	3·156	−0·4	·463	4·0	6·097	8·5	·291	13·0	11·162
·3	·204	·8	·181	·3	·497	·1	·140	·6	·347	·1	·235
·2	·223	·7	·206	·2	·531	·2	·183	·7	·404	·2	·309
·1	·242	·6	·231	·1	·565	·3	·226	·8	·461	·3	·383
−9·0	·261	·5	·257	−0·0	4·600	·4	·270	8·9	·517	·4	·456
−8·9	2·280	−4·4	·283	+0·0	4·600	4·5	·313	9·0	8·574	13·5	·530
·8	·299	·3	·309	·1	·633	·6	·357	·1	·632	·6	·605
·7	·318	·2	·335	·2	·667	·7	·401	·2	·690	·7	·681
·6	·337	·1	·361	·3	·700	·8	·445	·3	·748	·8	·757
·5	·356	−4·0	·387	·4	·733	4·9	·490	·4	·807	13·9	·832
−8·4	·376	−3·9	3·414	0·5	·767	5·0	6·534	9·5	·865	14·0	11·908
·3	·396	·8	·441	·6	·801	·1	·580	·6	·925	·1	·986
·2	·416	·7	·468	·7	·836	·2	·625	·7	·985	·2	12·064
·1	·436	·6	·495	·8	·871	·3	·671	·8	9·045	·3	·142
−8·0	·456	·5	·522	0·9	·905	·4	·717	9·9	·105	·4	·220
−7·9	2·477	−3·4	·550	1·0	4·940	5·5	·763	10·0	9·165	14·5	·298
·8	·498	·3	·578	·1	·975	·6	·810	·1	·227	·6	·378
·7	·519	·2	·606	·2	5·011	·7	·857	·2	·288	·7	·458
·6	·540	·1	·634	·3	·047	·8	·904	·3	·350	·8	·538
·5	·561	−3·0	·662	·4	·082	5·9	·951	·4	·412	14·9	·619
−7·4	·582	−2·9	3·691	1·5	·118	6·0	6·998	10·5	·474	15·0	12·699
·3	·603	·8	·720	·6	·155	·1	7·047	·6	·537	·1	·781
·2	·624	·7	·749	·7	·191	·2	·095	·7	·601	·2	·864
·1	·645	·6	·778	·8	·228	·3	·144	·8	·665	·3	·947
−7·0	·666	·5	·807	1·9	·265	·4	·193	10·9	·728	·4	13·029
−6·9	2·688	−2·4	·836	2·0	5·302	6·5	·242	11·0	9·792	15·5	·112
·8	·710	·3	·865	·1	·340	·6	·292	·1	·857	·6	·197
·7	·732	·2	·895	·2	·378	·7	·342	·2	·923	·7	·281
·6	·754	·1	·925	·3	·416	·8	·392	·3	·989	·8	·366
·5	·776	−2·0	·955	·4	·454	6·9	·442	·4	10·054	15·9	·451
−6·4	·798	−1·9	3·985	2·5	·491	7·0	7·492	11·5	·120	16·0	13·536
·3	·821	·8	4·016	·6	·530	·1	·544	·6	·187	·1	·623
·2	·844	·7	·047	·7	·569	·2	·595	·7	·255	·2	·710
·1	·867	·6	·078	·8	·608	·3	·647	·8	·322	·3	·797
−6·0	·890	·5	·109	2·9	·647	·4	·699	11·9	·389	·4	·885
−5·9	2·914	−1·4	·140	3·0	5·687	7·5	·751	12·0	10·457	16·5	·972
·8	·938	·3	·171	·1	·727	·6	·804	·1	·526	·6	14·062
·7	·962	·2	·203	·2	·767	·7	·857	·2	·596	·7	·151
·6	·986	·1	·235	·3	·807	·8	·910	·3	·665	·8	·241
·5	3·010	1·0	·267	·4	·848	7·9	·964	·4	·734	16·9	·331

TABLE I (*continued*).

Pressure of Aqueous Vapour—*continued.*

°	mm.	°	mm.	°	mm.	°	mm.	°	mm.	°	mm.
17·0	14 421	20·0	17·391	23·0	20·888	26·0	24·988	29·0	29·782	32·0	35·359
·1	·513	·1	·500	·1	21·016	·1	25·138	·1	·956	·1	·559
·2	·605	·2	·608	·2	·144	·2	·288	·2	30·131	·2	·760
·3	·697	·3	·717	·3	·272	·3	·438	·3	·305	·3	·962
·4	·790	·4	·826	·4	·400	·4	·588	·4	·479	·4	36·165
17·5	·882	20·5	·935	23·5	·528	26·5	·758	29·5	·654	32·5	·370
·6	·977	·6	18·047	·6	·659	·6	·891	·6	·833	·6	·576
·7	15 072	·7	·159	·7	·790	·7	26·045	·7	31·011	·7	·783
·8	·167	·8	·271	·8	·921	·8	·198	·8	·190	·8	·991
17·9	·262	20·9	·38[illegible]	23·9	22·07[illegible]	26·9	·357	29·9	·369	32·9	37·200
18·0	15·357	21·0	18·495	24·0	22·184	27·0	26·505	30·0	31·548	33·0	37·410
·1	·454	·1	·610	·1	·319	·1	·663	·1	·729	·1	·621
·2	·552	·2	·724	·2	·453	·2	·820	·2	·911	·2	·832
·3	·650	·3	·839	·3	·588	·3	·978	·3	32 094	·3	38·045
·4	·747	·4	·954	·4	·723	·4	27·136	·4	·278	·4	·258
18·5	·845	21·5	19·069	24·5	·858	27·5	·294	30·5	·463	33·5	·473
·6	·945	·6	·187	·6	·996	·6	455	·6	·650	·6	·689
·7	16·045	·7	·305	·7	23·135	·7	·617	·7	·837	·7	·906
·8	145	·8	·423	·8	·273	·8	·778	·8	33·026	·8	39·124
18·9	·246	21·9	·541	24·9	·411	27·9	·939	30·9	·215	33·9	·344
19·0	16·346	22 0	19 659	25·0	23 550	28·0	28·101	31·0	33·405	34·0	39·565
·1	·449	·1	780	·1	·692	·1	·267	·1	·596	·1	·786
·2	·552	·2	·901	2	·834	·2	·433	·2	·787	·2	40·007
·3	·655	·3	20·022	·3	·976	·3	·599	·3	·980	·3	·230
·4	·758	·4	·143	·4	24·119	·4	·765	4	34·174	·4	·455
19·5	·861	22·5	·265	25·5	·261	28·5	·941	31·5	·368	34·5	·680
·6	·967	·6	·389	·6	·406	·6	29·101	·6	·564	·6	·907
·7	17·073	7	·514	7	·552	·7	·271	7	·761	·7	41·135
·8	·179	·8	·639	·8	·697	·8	·441	·8	·959	·8	·364
19·9	·285	22·9	·763	25·9	·842	28·9	·612	31·9	35·159	34·9	·595
										35·0	·827

TABLE II.

Density of Mercury.

In grams per c.c. Hydrogen scale of temp. (See Chappuis Trav. et Mem. Bur. Intl, **13**, 1907.)

Temp.	0.	2.	4.	6.	8	10.	12	14.	16.	18.
	13	13	13	13	13	13	13	13	13	13
− 20° C	·6450	·6400	·6351	·6301	·6251	·6202	·6152	·6103	·6053	·6004
0	·5955	5905	·5856	·5806	5757	·5708	·5659	·5609	·5560	·5511
20	·5462	·5413	·5361	·5315	·5266	5217	·5168	5119	5070	·5022
40	·4973	·4924	·4875	·4826	·4778	·4729	·4680	·4632	·4583	4534
60	4486	·4437	·4389	·4340	·4292	·4243	·4195	·4146	·4098	·4050
80	·4001	·3953	3904	·3856	·3808	·3759	·3711	·3663	·3615	·3566

	0	20	40	60	80	100	120	140	160	180
100	13·35[illegible]8	13·304	13 257	13·[illegible]09	13·162	13·115	13·068	13·021	12·976	12·927
300	12·881	12·834	12·787	12 740	—	—	—	—	—	—

TABLE III.

TABLE for Correction of Volumes of Gases for Temperature, according to the Formula $V^1 = \frac{V \times B}{760 \times (1+\delta t)}$.

$1 + \delta t$ from 0° to 30°. $\delta = 0·003665$.

t.	1+δt.	Log. (1+δt)	t.	1+δt	Log. (1+δt).	t	1+δt.	Log. (1+δt).
0·0	1·0000000	0·000 0000	5·0	1·0183250	0·007 8864	10·0	1·0366500	0·015 6321
·1	1·0003665	1591	·1	1·0186915	0·008 0427	·1	1·0370165	7857
·2	1·0007330	3182	·2	1·0190580	1989	·2	1·0373830	9391
·3	1·0010995	4772	·3	1·0194245	4551	·3	1·0377495	0·016 0925
·4	1·0014660	6362	·4	1·0197910	5112	·4	1·0381160	2459
0·5	1·0018325	7951	5·5	1·0201575	6672	10·5	1·0384825	3992
·6	1·0021990	9540	·6	1·0205240	8232	·6	1·0388490	5524
·7	1·0025655	0·001 1128	·7	1·0208905	9791	·7	1·0392155	7056
·8	1·0029320	2715	·8	1·0212570	0·009 1350	·8	1·0395820	8588
·9	1·0032985	4302	5·9	1·0216235	2909	10·9	1·0399485	0·017 0118
1·0	1·0036650	0·001 5888	6·0	1·0219900	0·009 4466	11·0	1·0403150	0·017 1648
·1	1·0040315	7473	·1	1·0223565	6024	·1	1·0406815	3178
·2	1·0043980	9058	·2	1·0227230	7580	·2	1·0410480	4708
·3	1·0047645	0·002 0643	·3	1·0230895	9136	·3	1·0414145	6236
·4	1·0051310	2227	·4	1·0234560	0·010 0692	·4	1·0417810	7764
1·5	1·0054975	3810	6·5	1·0238225	2247	11·5	1·0421475	9292
·6	1·0058640	5393	·6	1·0241890	3801	·6	1·0425140	0·018 0819
·7	1·0062305	6974	·7	1·0245555	5355	·7	1·0428805	2346
·8	1·0065970	8556	·8	1·0249220	6908	·8	1·0432470	3871
1·9	1·0069635	0·003 0137	6·9	1·0252885	8461	11·9	1·0436135	5397
2·0	1·0073300	0·003 1718	7·0	1·0256550	0·011 0013	12·0	1·0439800	0·018 6922
·1	1·0076965	3298	·1	1·0260215	1565	·1	1·0443465	8446
·2	1·0080630	4877	·2	1·0263880	3116	·2	1·0447130	9970
·3	1·0084295	6455	·3	1·0267545	4666	·3	1·0450795	0·019 1493
·4	1·0087960	8033	·4	1·0271210	6216	·4	1·0454460	3016
2·5	1·0091625	9611	7·5	1·0274875	7765	12·5	1·0458125	4538
·6	1·0095290	0·004 1188	·6	1·0278540	9314	·6	1·0461790	6060
·7	1·0098955	2764	·7	1·0282205	0·012 0863	·7	1·0465455	7581
·8	1·0102620	4340	·8	1·0285870	2410	·8	1·0469120	9102
2·9	1·0106285	5916	7·9	1·0289535	3957	12·9	1·0472785	0·020 0622
3·0	1·0109950	0·004 7490	8·0	1·0293200	0·012 5504	13·0	1·0476450	0·020 2141
·1	1·0113615	9064	·1	1·0296865	7050	·1	1·0480115	3660
·2	1·0117280	0·005 0638	·2	1·0300530	8596	·2	1·0483780	5179
·3	1·0120945	2211	·3	1·0304195	0·013 0141	·3	1·0487445	6697
·4	1·0124610	3783	·4	1·0307860	1685	·4	1·0491110	8214
3·5	1·0128275	5355	8·5	1·0311525	3229	13·5	1·0494775	9731
·6	1·0131940	6926	·6	1·0315190	4772	·6	1·0498440	0·021 1248
·7	1·0135605	8497	·7	1·0318855	6315	·7	1·0502105	2764
·8	1·0139270	0·006 0067	·8	1·0322520	7857	·8	1·0505770	4279
3·9	1·0142935	1636	8·9	1·0326185	9399	13·9	1·0509435	5794
4·0	1·0146600	0·006 3205	9·0	1·0329850	0·014 0940	14·0	1·0513100	0·021 7308
·1	1·0150265	4774	·1	1·0333515	2481	·1	1·0516765	8822
·2	1·0153930	6342	·2	1·0337180	4021	·2	1·0520430	0·022 0335
·3	1·0157595	7909	·3	1·0340845	5560	·3	1·0524095	1848
·4	1·0161260	9476	·4	1·0344510	7099	·4	1·0527760	3360
4·5	1·0164925	0·007 1042	9·5	1·0348175	8638	14·5	1·0531425	4871
·6	1·0168590	2607	·6	1·0351840	0·015 0175	·6	1·0535090	6382
·7	1·0172255	4172	·7	1·0355505	1713	·7	1·0538755	7893
·8	1·0175920	5737	·8	1·0359170	3256	·8	1·0542420	9408
4·9	1·0179585	7301	9·9	1·0362835	4786	14·9	1·0546085	0·023 0193

TABLE III (*continued*).

TABLE for Correction of Volumes of Gases—*continued*.

t.	1 + δt.	Log. (1 + δt).	t.	1 + δt.	Log. (1 + δt).	t.	1 + δt.	Log. (1 + δt)
15°·0	1·0549750	0·023 2422	20°·0	1·0730000	0·030 7211	25°·0	1·0916250	0·038 0734
·1	1·0553415	3930	·1	1·0736665	8694	·1	1·0919915	2192
·2	1·0557080	5438	·2	1·0740330	0·031 0176	·2	1·0923580	3650
·3	1·0560745	6946	·3	1·0743995	1658	·3	1·0927245	5107
·4	1·0564410	8452	·4	1·0747660	3139	·4	1·0930910	6563
15·5	1·0568075	9959	20·5	1·0751325	4620	25·5	1·0934575	8019
·6	1·0571740	0·024 1465	·6	1·0754990	6100	·6	1·0938240	9474
·7	1·0575405	2970	·7	1·0758655	7580	·7	1·0941905	0·039 0929
·8	1·0579070	4475	·8	1·0762320	9059	·8	1·0945570	2384
15·9	1·0582735	5979	20·9	1·0765985	0·032 0538	·9	1·0949235	3838
16·0	1·0586400	0·024 7483	21·0	1·0769650	0·032 2016	26·0	1 0952900	0·039 5291
·1	1·0590065	8986	·1	1·0773315	3498	·1	1·0956565	6745
·2	1·0593730	0·025 0489	·2	1·0776980	4971	·2	1·0960230	8197
·3	1·0597395	1991	·3	1·0780645	6447	·3	1·0963895	9649
·4	1·0601060	3493	·4	1·0784310	7921	·4	1·0967560	0·040 1101
16·5	1·0604725	4994	21·5	1·0787975	9399	26·5	1·0971225	2551
·6	1·0608390	6495	·6	1·0791640	0·033 0874	·6	1·0974890	4002
·7	1·0612055	7995	·7	1·0795305	2349	·7	1·0978555	5452
·8	1·0615720	9495	·8	1 0798970	3823	·8	1·0982220	6901
16·9	1·0619385	0·026 0994	21·9	1·0802635	5298	·9	1·0985885	8351
17·0	1·0623050	0·026 2492	22·0	1·0806300	0·033 6771	27·0	1·0989550	0·040 9800
·1	1·0626715	3990	·1	1·0809965	8243	·1	1·0993215	0·041 1247
·2	1·0630380	5488	·2	1·0813630	9715	·2	1·0996880	2695
·3	1·0634045	6985	·3	1·0817295	0·034 1186	·3	1·1000545	4143
·4	1·0637710	8482	·4	1·0820960	2658	·4	1·1004210	5589
17·5	1 0641375	9978	22·5	1·0824625	4129	27·5	1·1007875	7036
·6	1·0645040	0·027 1473	·6	1·0828290	5598	·6	1·1011540	8481
·7	1·0648705	2968	·7	1·0831955	7069	·7	1·1015205	9926
·8	1·0652370	4462	·8	1 0835620	8538	·8	1·1018870	0·012 1371
17·9	1·0656035	5956	22 9	1·0839285	0·035 0006	·9	1·1022535	2815
18·0	1·0659700	0·027 7450	23·0	1·0842950	0·035 1475	28·0	1·1026200	0·042 4259
·1	1·0663365	8943	·1	1·0846615	2942	·1	1·1029865	5702
·2	1·0667030	0·028 0435	·2	1·0850280	4409	·2	1·1033530	7145
·3	1·0670695	1927	·3	1·0853945	5876	·3	1·1037195	8587
·4	1·0674360	3418	·4	1·0857610	7342	·4	1·1040860	0·043 0029
18·5	1·0678025	4909	23·5	1·0861275	8808	28·5	1·1044525	1471
·6	1·0681690	6400	·6	1·0864940	0·036 0273	·6	1·1048190	2911
·7	1·0685355	7889	·7	1·0868605	1738	·7	1·1051855	4352
·8	1·0689020	9379	·8	1·0872270	3202	·8	1·1055520	5792
18·9	1·0692685	0 029 0868	23·9	1·0875935	4666	·9	1·1059185	7231
19·0	1·0696350	0·029 2356	24·0	1·0879600	0·036 6129	29 0	1·1062850	0·043 8671
·1	1·0700015	3844	·1	1·0883265	7592	·1	1·1066515	0·044 0109
·2	1·0703680	5331	·2	1·0886930	9054	·2	1·1070180	1546
·3	1·0707345	6818	·3	1·0890595	0·037 0517	·3	1·1073845	2985
·4	1·0711010	8304	·4	1·0894260	1978	·4	1·1077510	4422
19·5	1·0714675	9790	24·5	1·0897925	3438	29·5	1·1081175	5858
·6	1·0718340	0 030 1275	·6	1·0901590	4899	·6	1·1084840	7295
·7	1 0722005	2760	·7	1·0905255	6359	·7	1·1088505	8730
·8	1·0725670	4244	·8	1·0908920	7817	·8	1·1092170	0·045 0165
19 9	1 0729335	5728	·9	1·0912585	9277	·9	1·1095835	1600
						30·0	1·1099500	0·045 3035

TABLE

Gas Volume

The numbers of this table give the volumes of gas saturated with water vapour at different 30 inches of mercury. They are calculated from the formula $V = \frac{459\cdot4+t}{17\cdot61\,(h-a)}$, where V is at t°, and t the temperature on

TEMPERATURE—FAHR.

BAROMETER—INCHES OF MERCURY.	40°	42°.	44°.	46°.	48°	50°.	52°.	54°.	56°.	57°	58°.	59°.	60°.	61°.	62°.
28·0	1·022	1·026	1·031	1·036	1·041	1·046	1·051	1·057	1·062	1·065	1·067	1·070	1·073	1·076	1·075
28·1	1·018	1·023	1·027	1·032	1·037	1·042	1·048	1·053	1·058	1·061	1·063	1·066	1·069	1·072	1·071
28·2	1·014	1·019	1·024	1·029	1·034	1·039	1·044	1·049	1·054	1·057	1·060	1·062	1·065	1·068	1·071
28·3	1·011	1·015	1·020	1·025	1·030	1·035	1·040	1·045	1·050	1·053	1·056	1·059	1·061	1·064	1·067
28·4	1·007	1·012	1·017	1·021	1·026	1·031	1·036	1·042	1·047	1·049	1·052	1·055	1·057	1·060	1·063
28·5	1·003	1·008	1·013	1·018	1·023	1·028	1·033	1·038	1·043	1·046	1·048	1·051	1·054	1·056	1·059
28·6	1·000	1·005	1·009	1·014	1·019	1·024	1·029	1·034	1·039	1·042	1·045	1·047	1·050	1·053	1·055
28·7	·996	1·001	1·006	1·011	1·015	1·020	1·025	1·030	1·036	1·038	1·041	1·044	1·046	1·049	1·052
28·8	·993	·997	1·002	1·007	1·012	1·017	1·022	1·027	1·032	1·035	1·037	1·040	1·043	1·045	1·048
28·9	·989	·994	·999	1·004	1·008	1·013	1·018	1·023	1·028	1·031	1·034	1·036	1·039	1·042	1·044
29·0	·986	·991	·995	1·000	1·005	1·010	1·015	1·020	1·025	1·027	1·030	1·033	1·035	1·038	1·041
29·1	·983	·987	·992	·997	1·001	1·006	1·011	1·016	1·021	1·024	1·026	1·029	1·032	1·034	1·037
29·2	·979	·984	·988	·993	·998	1·003	1·008	1·013	1·018	1·020	1·023	1·026	1·028	1·031	1·033
29·3	·976	·980	·985	·990	·994	·999	1·004	1·009	1·014	1·017	1·019	1·022	1·024	1·027	1·030
29·4	·972	·977	982	·986	·991	·996	1·001	1·006	1·011	1·013	1·016	1·018	1·021	1·023	1·026
29·5	·969	·974	·978	·983	·988	·992	·997	1·002	1·007	1·010	1·012	1·015	1·017	1·020	1·023
29·6	·966	·970	·975	·980	·984	·989	·994	·999	1·004	1·006	1·009	1·011	1·014	1·016	1·019
29·7	·963	·967	·972	·976	·981	·986	·990	·995	1·000	1·003	1·005	1·008	1·010	1·013	1·016
29·8	·959	·964	·968	·973	·978	·982	987	·992	·997	·999	1·002	1·004	1·007	1·009	1·012
29·9	·956	·960	·965	·970	·974	·979	·984	·988	·993	·996	·998	1·001	1·003	1·006	1·009
30·0	·953	·957	·962	·966	·971	·976	·980	·985	·990	·992	·995	·998	1·000	1·003	1·005
30·1	·950	·954	·959	·963	·968	·972	·977	·982	·987	·989	·992	·994	·997	·999	1·002
30·2	·946	·951	·955	·960	·964	·969	·974	·979	·983	·986	·988	·991	·993	·996	·998
30·3	·943	·948	·952	·957	·961	·966	·970	·975	·980	·982	·985	·987	·990	·992	·995
30·4	·940	·945	·949	·953	·958	·963	·967	·972	·977	·979	·982	·984	·987	·989	·992
30·5	·937	·941	·946	·950	·955	·959	·964	·969	·974	·976	·978	·981	·983	·986	·988
30·6	·934	·938	·943	·947	·952	·956	·961	·966	·970	·973	·975	·978	·980	·983	·985
30·7	·931	·935	·940	·944	·949	·953	·958	·962	·967	·970	·972	·974	·977	·979	·982
30·8	·928	·932	·937	·941	·945	·950	·955	·959	·964	·966	·969	·971	·974	·976	·979
30·9	·925	·929	·933	·938	·942	·947	·951	·956	·961	·963	·966	·968	·970	973	·975
31·0	·922	·926	·930	·935	·939	·944	·948	·953	·958	·960	·962	·965	·967	·970	·972

IV.

Factors.

temperatures and pressures corresponding to unit volume of saturated gas at 60° Fahr. and the volume, *h* the pressure of the gas in inches of mercury, *a* the vapour pressure of water the Fahrenheit scale.

BAROMETER—INCHES OF MERCURY.

	TEMPERATURE- FAHR.														
	63°.	64°.	65°.	66°.	67°.	68°	69°.	70°.	72°.	74°.	76°.	78°.	80°	82°.	84°.
28·0	1·081	1·084	1·087	1·090	1·093	1·096	1·099	1·102	1·108	1·115	1·121	1·128	1·135	1·142	1·149
28·1	1·077	1·080	1·083	1·086	1·089	1·092	1·095	1·098	1·104	1·111	1·117	1·124	1·131	1·138	1·145
28·2	1·074	1·076	1·079	1·082	1·085	1·088	1·091	1·094	1·100	1·107	1·113	1·120	1·127	1·134	1·141
28·3	1·070	1·072	1·075	1·078	1·081	1·084	1·087	1·090	1·096	1·103	1·109	1·116	1·123	1·130	1·137
28·4	1·066	1·069	1·071	1·074	1·077	1·080	1·083	1·086	1·092	1·099	1·105	1·112	1·118	1·125	1·133
28·5	1·062	1·065	1·068	1·070	1·073	1·076	1·079	1·082	1·088	1·095	1·101	1·108	1·114	1·121	1·128
28 6	1·058	1·061	1·064	1·067	1·070	1·072	1·075	1·078	1·084	1·091	1·097	1·104	1·110	1·117	1·124
28·7	1·054	1·057	1·060	1·063	1·066	1·069	1·072	1·075	1·081	1·087	1·093	1·100	1·106	1·113	1·120
28·8	1·051	1·053	1·056	1·059	1·062	1·065	1·068	1·071	1·077	1·083	1·089	1·096	1·102	1·109	1·116
28·9	1·047	1·050	1·053	1·055	1·058	1·061	1·064	1·067	1·073	1·079	1·085	1·092	1·098	1·105	1·112
29·0	1·043	1·046	1·049	1·052	1·054	1·057	1·060	1·063	1·069	1·075	1·081	1·088	1·094	1·101	1·108
29 1	1·040	1·042	1·045	1·048	1·051	1·054	1·056	1·059	1·065	1·071	1·078	1·084	1·091	1·097	1·104
29·2	1·036	1·039	1·041	1·044	1·047	1·050	1·053	1·056	1·062	1·068	1·074	1·080	1·087	1·093	1·100
29·3	1·032	1·035	1·038	1·041	1·043	1·046	1·049	1·052	1·058	1·064	1·070	1·076	1·083	1·090	1·096
29 4	1·029	1·032	1·034	1·037	1·040	1·043	1·045	1·048	1·054	1·060	1·066	1·073	1·079	1·086	1·092
29·5	1·025	1·028	1·031	1·033	1·036	1·039	1·042	1·045	1·050	1·056	1·063	1·069	1·075	1·082	1·089
29·6	1·022	1·024	1·027	1·030	1·033	1·035	1·038	1·041	1·047	1·053	1·059	1·065	1·071	1·078	1·085
29·7	1·018	1·021	1·024	1·026	1·029	1·032	1·035	1·037	1·043	1·049	1·055	1·061	1·068	1·074	1·081
29 8	1·015	1·017	1·020	1·023	1·025	1·028	1·031	1·034	1·040	1·046	1·052	1·058	1·064	[illegible]	1·077
29·9	1·011	1·014	1·017	[illegible]	1·022	1·025	1·028	1·030	1·036	1·042	1·048	1·054	1·060	1·067	1·073
30·0	1·008	1·010	1·013	1·016	1·019	1·021	1·024	1·027	1·033	1·038	1·044	1·050	1·057	1·063	1·070
30 1	1·004	1·007	1·010	1·012	1·015	1·018	1·021	1·023	1·029	1·035	1·041	1·047	1·053	1·059	1·066
30 2	1·001	1·004	1·006	1·009	1·012	1·014	1·017	1·020	1·025	1·031	1·037	1·043	1·049	1·056	1·062
30·3	·998	1·000	1·003	1·006	1·008	1·011	1·014	1·016	1·022	1·028	1·034	1·040	1·046	1·052	1·059
30·4	·994	·997	1·000	1·002	1·005	1·007	1·010	1·013	1·019	1·024	1·030	1·036	1·042	1·049	1·055
30·5	·991	·994	·996	·999	1·001	1·004	1·007	1·010	1·015	1·021	1·027	1·033	1·039	1·045	1·052
30·6	·988	·990	·993	·995	·998	1·001	1·003	1·006	1·012	1·017	1·023	1·029	1·035	1·042	1·048
30·7	·984	·987	·990	·992	·995	·997	1·000	1·003	1·008	1·014	1·020	1·026	1·032	1·038	1·044
30·8	·981	·984	·986	·989	·991	·994	·997	1·000	1·005	1·011	1·016	1·022	1·028	1·035	1·041
30·9	·978	·980	·983	·986	·988	·991	·993	·996	1·002	1·007	1·013	1·019	1·025	1·031	1·037
31·0	·975	·977	·980	·982	·985	·988	·990	·993	·998	1·004	1·010	1·015	1·021	1·028	1·034

TABLE

Logarithms of Gas Volume Factors, being

BAROMETER—INCHES OF MERCURY.	THERMOMETER—FAHR. 40°.	42°.	44°.	46°.	48°.	50°.	52°.	54°.	56°.	57°.	58°.	59°.	60°.	61°.	62°.
28·0	·0092	·0113	0133	0154	·0175	·0196	·0217	·0239	·0261	·0272	·0283	·0294	·0305	·0316	·0328
28·1	·0077	·0097	·0118	·0138	·0159	·0181	·0202	·0223	·0245	·0256	·0267	·0278	·0289	·0301	·0312
28·2	·0061	·0081	·0102	·0123	·0144	·0165	·0186	·0208	·0229	·0240	·0251	·0263	0274	·0285	·0296
28·3	·0046	·0066	·0086	·0107	·0128	·0149	·0170	·0192	·0214	·0225	·0236	·0247	·0258	·0269	·0281
28·4	·0030	·0050	·0071	·0092	·0113	·0134	·0155	·0176	·0198	·0209	·0220	0231	·0242	·0254	·0265
28·5	·0015	·0035	·0055	·0076	0097	·0118	·0139	·0161	·0183	·0194	0205	·0216	·0227	·0238	·0250
28·6	$\bar{1}$·9999	·0020	·0040	·0061	·0082	·0103	·0124	0145	0167	·0178	·0189	0200	·0211	·0223	·0234
28·7	·9984	0004	·0024	·0046	·0066	·0087	·0109	·0130	·0152	0163	·0174	·0185	·0196	·0207	0219
28·8	·9969	$\bar{1}$·9989	·0010	0030	0051	·0072	0093	·0115	0136	·0147	·0158	·0169	0181	·0192	·0203
28·9	·9954	·9974	$\bar{1}$·9994	·0015	·0036	·0057	0078	0100	0121	·0132	·0143	·0154	·0165	·0176	·0188
29·0	.9939	·9959	·9979	·0000	·0021	·0042	·0063	0084	·0106	0117	·0128	·0139	·0150	·0161	·0173
29·1	.9923	·9944	·9964	$\bar{1}$·9985	·0006	·0027	·0048	·0069	·0091	·0102	·0113	·0124	·0135	·0146	·0157
29·2	·9908	·9929	·9949	9970	$\bar{1}$·9990	·0011	·0033	·0054	0076	·0086	·0097	·0109	·0120	·0131	·0142
29·3	·9893	·9914	·9934	·9955	·9975	$\bar{1}$·9996	·0018	·0039	·0061	·0071	·0082	·0093	·0105	·0116	·0127
29·4	·9879	·9899	[illegible]	·9940	·9961	·9981	0003	·0024	·0046	·0056	·0067	·0078	·0089	·0101	·0112
29·5	·9864	·9884	·9904	·9925	·9946	·9967	$\bar{1}$·9988	·0009	0031	·0041	·0052	0063	·0074	·0085	·0097
29·6	9849	·9869	·9889	·9910	·9931	·9952	9973	$\bar{1}$·9994	·0016	·0026	·0037	·0048	·0059	·0071	·0082
29·7	·9834	·9854	·9875	9895	·9916	9937	9958	·9979	·0001	0011	·0022	·0033	·0045	·0056	·0067
29·8	·9819	9839	·9860	·9880	·9901	·9922	·9943	·9964	$\bar{1}$·9986	$\bar{1}$·9997	·0008	·0018	·0030	·0041	·0052
29·9	·9805	·9825	9845	·9866	·9886	·9907	·9928	·9950	·9971	·9982	$\bar{1}$·9993	·0004	·0015	·0026	·0037
30·0	·9790	·9810	·9831	·9851	9872	·9893	9914	·9935	·9956	·9967	·9978	$\bar{1}$·9989	·0000	·0011	·0022
30·1	·9775	·9796	·9816	·9836	9857	·9878	·9899	·9920	·9942	9953	·9963	·9974	$\bar{1}$·9985	$\bar{1}$·9996	·0008
30·2	·9761	·9781	·9801	9822	·9843	9863	·9884	·9906	·9927	·9938	·9949	·9960	·9971	·9982	$\bar{1}$·9993
30·3	·9746	·9767	·9787	·9807	·9828	·9849	·9870	·9891	·9913	·9923	·9934	·9945	·9956	·9967	·9978
30·4	·9732	·9752	·9772	9793	9814	·9834	·9855	9877	·9898	·9909	·9920	·9931	·9942	·9953	·9964
30·5	·9718	·9738	·9758	·9779	·9799	9820	·9841	·9862	·9884	·9894	·9905	·9916	·9927	·9938	·9949
30·6	·9703	·9723	·9744	·9764	9785	·9806	9827	9848	·9869	·9880	·9891	·9902	·9913	·9924	·9935
30·7	·9689	·9709	·9729	·9750	·9770	·9791	·9812	9833	·9855	·9865	·9876	·9887	·9898	·9909	·9920
30·8	9675	·9695	·9715	·9736	·9756	·9777	·9798	·9819	·9840	·9851	·9862	·9873	·9884	·9895	·9906
30·9	·9661	·9681	9701	·9721	·9742	·9763	9784	9805	·9826	·9837	·9848	·9859	·9870	·9880	·9892
31·0	·9646	·9666	·9687	·9707	·9728	·9749	·9769	·9791	·9812	·9823	9833	9844	·9855	·9866	·9877

V.

the Logarithms of the Numbers in Table IV.

BAROMETER—INCHES OF MERCURY.

	THERMOMETER—FAHR.														
	63°.	64°.	65°.	66°.	67°.	68°.	69°.	70°.	72°.	74°.	76°.	78°.	80°.	82°.	84°.
28·0	·0339	·0351	·0363	·0374	·0386	·0398	·0410	·0422	·0447	0472	·0497	·0523	·0550	·0577	·0605
28·1	·0324	·0335	·0347	·0358	·0370	·0382	·0394	·0406	·0431	·0456	·0481	·0507	·0534	·0561	·0589
28·2	·0308	·0319	·0331	·0343	·0354	·0366	·0378	·0390	·0415	·0440	·0465	·0491	·0518	·0545	·0572
28·3	·0292	·0304	·0315	·0327	·0339	·0350	·0362	·0375	0399	·0424	·0449	·0475	·0502	·0529	·0556
28·4	0277	·0288	·0300	·0311	·0323	·0335	·0347	·0359	·0383	·0408	·0434	·0460	·0486	·0513	·0540
28·5	·0261	·0272	·0284	·0296	·0307	·0319	·0331	·0343	·0368	·0393	·0418	·0444	·0470	·0497	·0525
28·6	·0245	·0256	·0268	·0280	·0292	·0304	·0316	·0328	·0352	·0377	·0402	·0428	·0454	·0481	·0509
28·7	·0230	·0241	·0253	·0265	·0276	0288	0300	0312	·0336	0361	·0386	·0412	·0439	·0466	·0493
28·8	·0215	0226	·0237	·0249	·0261	0273	·0284	·0297	·0321	·0346	0371	·0397	·0423	·0450	·0477
28·9	·0199	·0211	·0222	·0234	·0245	·0257	0269	·0281	·0305	·0330	·0355	·0381	·0407	·0434	·0461
29·0	·0184	·0195	·0207	·0218	·0230	·0242	·0254	0266	0290	·0315	·0340	·0366	·0392	·0419	·0446
29·1	0169	·0180	·0191	·0203	·0215	·0226	·0238	·0250	0275	·0299	·0324	·0350	·0376	·0403	·0430
29·2	·0153	·0165	·0176	·0188	·0199	·0211	·0223	0235	·0259	·0284	·0309	·0335	·0361	·0388	·0415
29·3	·0138	·0150	·0161	·0173	·0184	·0196	·0208	·0220	·0244	·0269	·0294	0319	·0345	·0372	·0399
29·4	0123	·0135	·0146	·0158	·0169	·0181	·0193	·0205	·0229	·0254	·0278	·0304	·0330	·0357	·0384
29·5	·0108	·0119	·0131	·0142	·0154	·0166	·0178	·0190	·0214	·0238	·0263	·0289	·0315	·0341	·0369
29 6	0093	·0104	·0116	·0127	·0139	·0151	·0163	·0175	0199	·0223	·0248	·0274	·0300	·0326	·0353
29 7	0078	·0090	·0101	·0112	·0124	·0136	·0148	·0160	·0184	0208	·0233	·0259	·0284	·0311	·0338
29·8	·0063	·0075	·0086	·0098	0109	0121	·0133	·0145	0169	·0193	·0218	·0243	·0269	·0296	·0323
29·9	·0049	·0060	·0071	·0083	0094	0106	·0118	·0130	·0154	·0178	·0203	·0228	·0254	·0281	·0308
30·0	·0034	·0045	·0056	·0068	·0079	0091	·0103	·0115	0139	0163	·0188	·0213	·0239	·0266	·0293
30 1	·0019	·0030	0042	·0053	·0065	·0076	·0088	·0100	·0124	·0148	·0173	·0198	·0224	·0251	·0278
30·2	·0004	·0016	·0027	·0038	·0050	·0062	·0073	·0085	·0109	·0134	·0158	·0184	·0209	·0236	·0263
30·3	$\bar{1}$·9990	·0001	·0012	·0024	·0035	·0047	·0059	0070	·0094	·0119	·0143	·0169	·0195	·0221	[illegible]
30·4	·9975	1·9986	$\bar{1}$·9998	0009	·0021	·0032	0044	·0056	·0080	·0104	·0129	·0154	·0180	·0206	·0233
30·5	·9961	·9972	·9983	1 9995	·0006	·0018	·0029	0041	0065	·0089	·0114	·0139	·0165	·0191	·0218
30·6	·9946	·9957	·9969	·9980	$\bar{1}$·9991	·0003	·0015	0027	·0050	·0075	0099	·0125	·0150	·0176	·0203
30·7	·9932	·9943	·9954	·9966	·9977	$\bar{1}$·9989	0000	0012	0036	·0060	·0085	·0110	·0136	·0162	·0188
30·8	·9917	·9928	·9940	9951	·9963	9974	$\bar{1}$ 9986	1·9998	0021	0046	·0070	·0095	·0121	·0147	·0174
30·9	9903	·9914	·9925	·9937	·9948	·9960	·9971	·9983	·0007	·0031	·0056	·0081	·0106	·0133	·0159
31·0	·9889	·9900	·9911	·9922	·9934	·9946	·9957	9969	$\bar{1}$ 9993	·0017	·0041	·0066	·0092	·0118	·0144

TABLE VI.

Table of Hardness, Parts in 100,000.

Volume of Soap Solution.	$CaCO_3$ per 100,000.	Volume of Soap Solution.	$CaCO_3$ per 100,000.	Volume of Soap Solution.	$CaCO_3$ per 100,000.	Volume of Soap Solution.	$CaCO_3$ per 100,000.
c.c.		c.c.		c.c.		c.c.	
—	—	4·0	4·57	8·0	10·30	12·0	16·43
—	—	1	·71	1	·45	1	·39
—	—	2	·86	2	·60	2	·75
—	—	3	5·00	3	·75	3	·90
—	—	4	·14	4	·90	4	17·06
—	—	5	·29	5	11·05	5	·22
—	—	6	·43	6	·20	6	·38
0·7	·00	7	·57	7	·35	7	·54
0·8	·16	8	·71	8	·50	8	·70
0·9	·32	9	·86	9	·65	9	·86
1·0	·48	5·0	6·00	9·0	·80	13·0	18·02
1	·63	1	·14	1	·95	1	·17
2	·79	2	·29	2	12·11	2	·33
3	·95	3	·43	3	·26	3	·49
4	1·11	4	·57	4	·41	4	·65
5	·27	5	·71	5	·56	5	·81
6	·43	6	·86	6	·71	6	·97
7	·56	7	7·00	7	·86	7	19·13
8	·69	8	·14	8	13·01	8	·29
9	·82	9	·29	9	·16	9	·44
2·0	·95	6·0	·43	10·0	·31	14·0	·60
1	2·08	1	·57	1	·46	1	·76
2	·21	2	·71	2	·61	2	·92
3	·34	3	·86	3	·76	3	20·08
4	·47	4	8·00	4	·91	4	·24
5	·60	5	·14	5	14·06	5	·40
6	·73	6	·29	6	·21	6	·56
7	·86	7	43	7	·37	7	71
8	·99	8	·57	8	·52	8	·87
9	3·12	9	·71	9	·68	9	21·03
3·0	·25	7·0	·86	11·0	·84	15·0	·19
1	·38	1	9·00	1	15·00	1	·35
2	·51	2	·14	2	·16	2	·51
3	·64	3	·29	3	·32	3	·68
4	·77	4	·43	4	·48	4	·85
5	·90	5	·57	5	·63	5	22·02
6	4·03	6	·71	6	·79	6	·18
7	·16	7	·86	7	·95	7	·35
8	·29	8	10·00	8	16·11	8	·52
3·9	·43	7·9	·15	11·9	·27	9	·69
—	—	—	—	—	—	16·0	·86

TABLE VII.

Oxygen Dissolved by Distilled Water. 5°-30° C.

(Roscoe and Lunt).[1]

Temp. °C.	c.c. Oxygen N.T.P. per litre Aq.	Diff. for 0 5° C.	Temp. °C.	c.c. Oxygen N.T.P. per litre Aq	Diff for 0·5° C.
5·0	8·68	--	18·0	6·54	0·07
5·5	8·58	0·10	18·5	6·47	0·07
6·0	8·49	0·09	19·0	6·40	0·06
6·5	8·40	0·09	19·5	6·34	0·06
7·0	8·31	0·09	20·0	6·28	0·06
7·5	8·22	0·09	20·5	6·22	0·06
8·0	8·13	0·09	21·0	6·16	0·06
8·5	8·04	0·09	21·5	6·10	0·06
9·0	7·95	0·09	22·0	6·04	0·05
9·5	7·86	0·09	22·5	5·99	0·05
10·0	7·77	0·09	23·0	5·94	0·05
10·5	7·68	0·08	23·5	5·89	0·05
11·0	7·60	0·08	24·0	5·81	0·04
11·5	7·52	0·08	24·5	5·80	0·04
12·0	7·44	0·08	25·0	5·76	0·04
12·5	7·36	0·08	25·5	5·72	0·04
13·0	7·28	0·08	26·0	5·68	0 04
13·5	7·20	0·08	26·5	5·64	0·04
14·0	7·12	0·08	27·0	5·60	0·03
14·5	7·04	0·08	27·5	5·57	0·03
15·0	6·96	0·08	28·0	5·54	0·03
15·5	6·89	0·07	28·5	5·51	0 03
16·0	6·82	0·07	29·0	5·18	0·03
16·5	6·75	0·07	29·5	5·45	0·02
17·0	6·68	0·07	30·0	5·43	—
17·5	6·61	0·07	—	--	—

In this table the results are calculated for aëration at an *observed* barometric pressure of 760 mm. When the observed pressure is *below* 760 mm. $\frac{1}{76}$ the value must be *subtracted* for every 10 mm. diff. The same value must be *added* when the pressure is *above* 760 mm.

TABLE VIII.

Amounts of Dissolved Oxygen in Distilled Water from 0°-30° C. (Bar. 760 mm.)[2]

Temperature ° C.	Oxygen (Parts per 100,000).	Temperature ° C.	Oxygen (Parts per 100,000).
0	1·42	16	0·98
1	1·39	17	0·96
2	1·36	18	0·94
3	1·32	19	0·92
4	1·28	20	0·90
5	1·24	21	0·88
6	1·22	22	0·87
7	1·19	23	0·85
8	1·17	24	0·84
9	1·14	25	0·82
10	1·11	26	0·81
11	1·09	27	0·80
12	1·07	28	0·80
13	1·04	29	0·79
14	1·02	30	0·78
15	1·00	---	—

---

[1] *J. C. S.*, 1889, 532.

[2] Calculated from Roscoe and Lunt's table from 5°-30° C. and from determinations by Winkler's process for the values given for 0° to 4° C.

TABLE XIX.—Dissolved Oxygen in Natural Waters.

The following Table gives the weight in grammes of oxygen absorbed by 100,000 c.c. of water of given Chlorine value and at stated temperature from a free dry atmosphere under pressure of 760 mm. of mercury and free of Carbon Dioxide.

C°	Cl=0	Cl=1	Cl=2	Cl=3	Cl=4	Cl=5	Cl=6	Cl=7	Cl=8	Cl=9	Cl=10	Cl=11	Cl=12	Cl=13	Cl=14	Cl=15	Cl=16	Cl=17	Cl=18	Cl=19	Cl=20
0	1·47	1·45	1·44	1·42	1·40	1·39	1·37	1·35	1·34	1·32	1·30	1·29	1·27	1·25	1·24	1·22	1·20	1·19	1·17	1·15	1·14
1	1·43	1·41	1·40	1·38	1·37	1·35	1·33	1·32	1·31	1·29	1·27	1·26	1·24	1·22	1·21	1·19	1·17	1·16	1·14	1·12	1·11
2	1·39	1·38	1·36	1·35	1·33	1·32	1·30	1·28	1·27	1·25	1·24	1·22	1·21	1·19	1·18	1·16	1·15	1·13	1·11	1·10	1·08
3	1·36	1·34	1·33	1·31	1·30	1·28	1·27	1·25	1·24	1·22	1·21	1·19	1·18	1·16	1·15	1·13	1·12	1·10	1·09	1·07	1·06
4	1·32	1·31	1·29	1·28	1·26	1·25	1·24	1·22	1·21	1·19	1·18	1·16	1·15	1·13	1·12	1·11	1·09	1·08	1·06	1·05	1·03
5	1·29	1·28	1·26	1·25	1·23	1·22	1·21	1·19	1·18	1·16	1·15	1·14	1·12	1·11	1·09	1·08	1·07	1·05	1·04	1·02	1·01
6	1·26	1·24	1·23	1·22	1·20	1·19	1·18	1·16	1·15	1·14	1·12	1·11	1·10	1·08	1·07	1·05	1·04	1·03	1·01	1·00	0·99
7	1·23	1·21	1·20	1·19	1·18	1·16	1·15	1·14	1·12	1·11	1·10	1·08	1·07	1·06	1·04	1·03	1·02	1·01	0·99	0·98	0·97
8	1·20	1·19	1·17	1·16	1·15	1·14	1·12	1·11	1·10	1·08	1·07	1·06	1·05	1·03	1·02	1·01	1·00	0·98	0·97	0·96	0·95
9	1·17	1·16	1·15	1·14	1·12	1·11	1·10	1·09	1·07	1·06	1·05	1·04	1·02	1·01	1·00	0·99	0·98	0·96	0·95	0·94	0·93
10	1·15	1·13	1·12	1·11	1·10	1·09	1·07	1·06	1·05	1·04	1·03	1·01	1·00	0·99	0·98	0·97	0·96	0·94	0·93	0·92	0·91
11	1·12	1·11	1·10	1·09	1·07	1·06	1·05	1·04	1·03	1·02	1·01	0·99	0·98	0·97	0·96	0·95	0·94	0·92	0·91	0·90	0·89
12	1·10	1·09	1·07	1·06	1·05	1·04	1·03	1·02	1·01	1·00	0·98	0·97	0·96	0·95	0·94	0·93	0·92	0·91	0·90	0·88	0·87
13	1·07	1·06	1·05	1·04	1·03	1·02	1·01	1·00	0·99	0·98	0·97	0·95	0·94	0·93	0·92	0·91	0·90	0·89	0·88	0·87	0·86
14	1·05	1·04	1·03	1·02	1·01	1·00	0·99	0·98	0·97	0·96	0·95	0·94	0·93	0·92	0·91	0·89	0·88	0·87	0·86	0·85	0·84
15	1·03	1·02	1·01	1·00	0·99	0·98	0·97	0·96	0·95	0·94	0·93	0·92	0·91	0·90	0·89	0·88	0·87	0·86	0·85	0·84	0·83
16	1·01	1·00	0·99	0·98	0·97	0·96	0·95	0·94	0·93	0·92	0·91	0·90	0·89	0·88	0·87	0·86	0·85	0·84	0·83	0·82	0·81
17	0·99	0·98	0·97	0·96	0·95	0·94	0·93	0·92	0·91	0·90	0·90	0·89	0·88	0·87	0·86	0·85	0·84	0·83	0·82	0·81	0·80
18	0·97	0·96	0·95	0·95	0·94	0·93	0·92	0·91	0·90	0·89	0·88	0·87	0·86	0·85	0·84	0·84	0·82	0·81	0·80	0·79	0·78
19	0·96	0·95	0·94	0·93	0·92	0·91	0·90	0·89	0·88	0·87	0·86	0·85	0·85	0·84	0·83	0·82	0·81	0·80	0·79	0·78	0·77
20	0·94	0·93	0·92	0·91	0·90	0·89	0·88	0·88	0·87	0·86	0·85	0·84	0·83	0·82	0·81	0·80	0·79	0·79	0·78	0·77	0·76
21	0·92	0·91	0·90	0·90	0·89	0·88	0·87	0·86	0·85	0·84	0·84	0·83	0·82	0·81	0·80	0·79	0·78	0·77	0·76	0·76	0·75
22	0·91	0·90	0·89	0·88	0·87	0·86	0·85	0·85	0·84	0·83	0·82	0·81	0·80	0·79	0·79	0·78	0·77	0·76	0·75	0·74	0·73
23	0·89	0·88	0·87	0·87	0·86	0·85	0·84	0·83	0·82	0·82	0·81	0·80	0·79	0·78	0·77	0·76	0·76	0·75	0·74	0·73	0·72
24	0·88	0·87	0·86	0·85	0·84	0·83	0·83	0·82	0·81	0·80	0·79	0·79	0·78	0·77	0·76	0·75	0·74	0·73	0·73	0·72	0·71
25	0·86	0·86	0·85	0·84	0·83	0·82	0·81	0·81	0·80	0·79	0·78	0·77	0·76	0·76	0·75	0·74	0·73	0·72	0·71	0·70	0·69
26	0·85	0·84	0·83	0·82	0·82	0·81	0·80	0·79	0·78	0·78	0·77	0·76	0·75	0·74	0·73	0·73	0·72	0·71	0·70	0·69	0·68
27	0·83	0·83	0·82	0·81	0·80	0·79	0·79	0·78	0·77	0·76	0·75	0·75	0·74	0·73	0·72	0·71	0·71	0·70	0·69	0·68	0·67
28	0·82	0·81	0·81	0·80	0·79	0·78	0·77	0·77	0·76	0·75	0·74	0·73	0·73	0·72	0·71	0·70	0·69	0·69	0·68	0·67	0·66
29	0·81	0·80	0·79	0·78	0·78	0·77	0·76	0·75	0·75	0·74	0·73	0·72	0·71	0·70	0·70	0·69	0·68	0·67	0·67	0·66	0·65
30	0·80	0·79	0·78	0·77	0·76	0·76	0·75	0·74	0·73	0·72	0·72	0·71	0·70	0·69	0·68	0·68	0·67	0·66	0·65	0·65	0·64

The above Table will enable the weight of dissolved oxygen per 100,000 c c. water to be converted into per cent. of saturation under the conditions of temperature and salinity stated. The salinity is given at the head of each column expressed in parts chlorine per 1000.

TABLE X.

Reduction of Cubic Centimetres of Nitrogen to Grammes.

Log. $\frac{0{\cdot}0012507}{(1+{\cdot}003665\,t)\,760}$ for each tenth of a degree from 0° to 30° C.

t.	0·0.	0·1.	0·2.	0·3.	0·4.	0·5.	0·6.	0·7.	0·8.	0·9.
° C.										
0	6·21634	618	602	586	570	554	539	523	507	491
1	475	459	443	427	411	395	379	363	347	332
2	317	301	285	269	253	237	221	205	189	174
3	159	143	127	112	096	080	065	049	033	018
4	002	986	970	955	939	923	908	892	876	861
5	6·20845	829	813	798	782	766	751	735	719	704
6	6·20689	673	658	642	627	611	596	580	565	549
7	534	518	503	487	472	456	441	425	410	394
8	379	364	348	333	317	302	286	271	255	240
9	225	210	194	179	163	148	132	117	101	086
10	071	056	040	025	009	994	979	963	948	932
11	6·19917	902	887	872	856	841	826	811	796	780
12	6·19765	750	735	720	704	689	674	659	644	628
13	613	598	583	568	552	537	522	507	492	476
14	461	446	431	416	401	386	371	356	341	325
15	310	295	280	265	250	235	220	205	190	174
16	159	144	129	114	099	084	069	054	039	024
17	009	994	979	964	949	934	919	904	889	874
18	6·18859	844	829	814	799	784	769	754	739	724
19	710	695	680	665	650	635	620	606	591	576
20	562	547	532	517	502	487	472	458	443	428
21	414	399	384	369	354	339	324	310	295	280
22	266	251	236	221	206	191	176	162	147	132
23	119	104	089	075	060	045	031	016	002	987
24	6·17973	958	943	929	914	899	885	870	856	841
25	827	812	797	783	768	753	739	724	710	695
26	681	666	651	637	622	607	593	578	564	549
27	536	521	507	492	478	463	449	434	420	405
28	391	376	362	347	333	318	304	289	275	260
29	247	232	218	203	189	175	160	146	131	117

TABLE XI.

Loss of Nitrogen by Evaporation of NH^3. With Sulphurous Acid.

Parts per 100,000.

N as NH^3.	Loss of N.	N as NH^3.	Loss of N.	N as NH^3	Loss of N.	N as NH^3.	Loss of N.	N as NH^3	Loss of N.	N as NH^3.	Loss of N.
5·0	1·741	3·9	1·425	2·8	·898	1·7	·370	·6	·145	·04	·009
4·9	1·717	3·8	1·378	2·7	·850	1·6	·338	5	·109	·03	·007
4·8	1·693	3 7	1·330	2·6	·802	1·5	·324	·4	·075	·02	·005
4·7	1·669	3·6	1·282	2·5	·754	1·4	·309	·3	·057	·01	·003
4·6	1·645	3·5	1·234	2·4	·706	1·3	·295	·2	·038	·008	·002
4·5	1·621	3·4	1·186	2·3	·658	1 2	·280	·1	·020	·007	·001
4·4	1·598	3·3	1·138	2·2	·610	1·1	·266	·09	·018	—	—
4·3	1·574	3·2	1·090	2·1	·562	1·0	·252	·08	·017	—	—
4·2	1·550	3·1	1 042	2·0	·514	·9	·237	·07	·015	—	—
4·1	1·521	3·0	·994	1·9	·466	·8	·217	·06	·013	—	—
4·0	1·473	2·9	·946	1·8	·418	·7	·181	·05	·011	—	—

TABLE XII.

Loss of Nitrogen by Evaporation of NH^3. With Hydric Metaphosphate.

Parts per 100,000.

Volume Evaporated.	N as NH^3.	Loss of N.	Volume Evaporated.	N as NH^3	Loss of N.	Volume Evaporated	N as NH^3	Loss of N	Volume Evaporated.	N as NH^3.	Loss of N.
100 c.c.	8·2	·482	100 c.c.	5 9	·385	100 c.c.	3·6	·281	100 c.c.	1·3	·142
—	8·1	·477	—	5·8	·381	—	3·5	·277	—	1·2	·136
—	8·0	·473	—	5·7	·377	—	3·4	·272	—	1·1	·129
—	7·9	·469	—	5·6	·373	—	3·3	·267	—	1·0	·123
—	7·8	·465	—	5 5	·368		3·2	·261	—	·9	·117
—	7·7	·461	—	5·4	·364	—	3·1	·255	—	·8	·111
—	7·6	·456	—	5·3	·360	-	3·0	·249	250 c.c.	·7	·088
—	7·5	·452	—	5·2	·356	—	2 9	·242	—	·6	·073
—	7·4	·448	—	5·1	·352	—	2·8	·236	—	·5	·061
—	7·3	·444	—	5·0	·347	—	2·7	·230	500 c.c.	·4	·049
—	7·2	·440	—	4·9	·343	—	2·6	·223	—	·3	·036
—	7·1	435	—	4·8	·338	—	2·5	·217	1000 c.c.	·2	·024
—	7·0	·431	—	4·7	·331	—	2·4	·211	—	·1	·012
—	6·9	·427	—	4·6	·329	—	2·3	·205	—	·09	·011
—	6·8	·423	—	4·5	·324	—	2·2	·198	—	·08	·010
—	6·7	·419	—	4·4	·319	—	2·1	·192	—	·07	·008
—	6·6	·414	—	4·3	·315	—	2·0	·186	—	·06	·007
—	6·5	·410	—	4·2	·310	—	1·9	·180	—	·05	·006
—	6·4	·406	—	4·1	·305	—	1·8	·173	—	·04	·005
—	6·3	402	—	4·0	·301	—	1·7	·167	—	·03	·004
—	6·2	·398	—	3·9	·296	—	1·6	·161	—	·02	·002
—	6·1	·394	—	3·8	·291	—	1·5	·154	—	·01	·001
—	6·0	·389	—	3·7	·286	—	1·4	·148	—	—	—

TABLE XIII.

Loss of Nitrogen by Evaporation of NH^3. With Sulphurous Acid.

Parts per 100,000.

NH^3.	Loss of N.	NH^3.	Loss of N.	NH^3	Loss of N.	NH^3.	Loss of N.	NH^3	Loss of N.	NH^3	Loss of N.
6·0	1·727	4·8	1·451	3·6	·977	2·4	·503	1·2	·250	·09	·014
5·9	1·707	4·7	1·411	3·5	·937	2·3	·463	1·1	238	·08	·013
5·8	1·688	4·6	1·372	3·4	·898	2·2	·424	1·0	·226	·07	·012
5·7	1·668	4·5	1·332	3·3	·858	2·1	·384	·9	·196	·06	·010
5·6	1·648	4·4	1·293	3·2	·819	2·0	·345	·8	·166	·05	·009
5·5	1·628	4·3	1·253	3·1	·779	1·9	·333	·7	·136	·04	·007
5·4	1·609	4·2	1·214	3·0	·740	1·8	·321	·6	·106	·03	·006
5·3	1·589	4·1	1·174	2·9	·700	1·7	·309	·5	·077	·02	·004
5·2	1·569	4·0	1·135	2·8	·661	1·6	·297	·4	·062	·01	·003
5·1	1·549	3·9	1·095	2·7	·621	1·5	·285	·3	·047	·009	·001
5·0	1·530	3·8	1·056	2·6	·582	1·4	·274	·2	·032	—	—
4·9	1·490	3·7	1·016	2·5	·542	1·3	·262	·1	·017	—	—

TABLE XIV.

Loss of Nitrogen by Evaporation of NH^3. With Hydric Metaphosphate.

Parts per 100,000.

Volume Evaporated.	NH^3.	Loss of N.	Volume Evaporated	NH^3.	Loss of N.	Volume Evaporated	NH^3.	Loss of N.	Volume Evaporated	NH^3.	Loss of N.
100 c.c.	10·0	·483	100 c.c.	7·2	·386	100 c.c.	4·4	·283	100 c.c.	1·6	·143
—	9·9	·480	—	7·1	·382	—	4·3	·279	—	1·5	·137
—	9·8	476	—	7·0	·379	—	4·2	·275	—	1·4	·132
—	9·7	·473	—	6·9	·375	—	4·1	·271	—	1·3	·127
—	9·6	·469	—	6·8	·372	—	4·0	·267	—	1·2	·122
—	9·5	·466	—	6·7	·368	—	3·9	·262	—	1·1	·117
—	9·4	·462	—	6·6	365	—	3·8	·257	—	1·0	·112
—	9·3	·459	—	6·5	·361	—	3·7	·252	250 c.c.	·9	·096
—	9·2	·455	—	6·4	·358	—	3·6	·247	—	·8	·080
—	9·1	·452	—	6·3	·354	—	3·5	·242	—	·7	·070
—	9·0	·448	—	6·2	·351	—	3·4	·236	—	·6	·060
—	8·9	·445	—	6·1	·348	—	3·3	·231	500 c.c.	·5	·050
—	8·8	·441	—	6·0	345	—	3·2	·226	—	·4	·040
—	8·7	·438	—	5·9	·341	—	3·1	·221	—	·3	·030
—	8·6	·434	—	5·8	·337	—	3·0	·216	1000 c.c.	·2	·020
—	8·5	·431	—	5·7	·333	—	2·9	·211	—	·1	·010
—	8·4	·428	—	5·6	·330	—	2·8	·205	—	·09	·009
—	8·3	·424	—	5·5	·326	—	2·7	·200	—	·08	·008
—	8·2	·421	—	5·4	·322	—	2·6	·195	—	·07	·007
—	8·1	·417	—	5·3	·318	—	2·5	·190	—	·06	·006
—	8·0	·414	—	5·2	·314	—	2·4	·184	—	·05	·005
—	7·9	·410	—	5·1	·310	—	2·3	·179	—	·04	·004
—	7·8	·407	—	5·0	·306	—	2·2	·174		·03	·003
—	7·7	·403	—	4·9	·302	—	2·1	·169	—	·02	·002
—	7·6	·400	—	4·8	·298	—	2·0	164	—	·01	·001
—	7·5	·396	—	4·7	·294	—	1·9	·158	—	—	—
—	7·4	·393	—	4·6	·291	—	1·8	153	—	—	—
—	7·3	·389	—	4·5	·287	—	1·7	·148	—	—	—

COEFFICIENTS AND LOGARITHMS FOR VOLUMETRIC ANALYSIS.

	Coefficients.			Logarithms.
Normal H_2SO_4	1 c.c. = 0·049038	grm.	H_2SO_4	$\bar{2}$·69053
	,, = 0·04803	,,	SO_4	$\bar{2}$·68151
	,, = 0·04003	,,	SO_3	$\bar{2}$·60239
Normal HCl	1 c.c. = 0·036468	,,	HCl	$\bar{2}$·56191
	,, = 0·03546	,,	Cl	$\bar{2}$·54974
Normal HNO_3	1 c.c. = 0·063018	,,	HNO_3	$\bar{2}$·79946
	,, = 0·06201	,,	NO_3	$\bar{2}$·79246
	,, = 0·05401	,,	N_2O_5	$\bar{2}$·73247
Normal $H_2C_2O_4$	1 c.c. = 0·063024	,,	$H_2C_2O_4$, $2OH_2$	$\bar{2}$·79951
	,, = 0·045008	,,	$H_2C_2O_4$	$\bar{2}$·65329
Normal Acid	1 c.c. = 0·017034	,,	NH_3	$\bar{2}$·23132
	,, = 0·03505	,,	NH_4HO	$\bar{2}$·54469
	,, = 0·01401	,,	N	$\bar{2}$·14644
	,, = 0·19088	,,	$Na_2B_4O_710H_2O$	$\bar{1}$·28076
	,, = 0·037043	,,	Ca2HO	$\bar{2}$·56871
	,, = 0·028035	,,	CaO	$\bar{2}$·44770
	,, = 0·050035	,,	$CaCO_3$	$\bar{2}$·69927
	,, = 0·085693	,,	BaH_2O_2	$\bar{2}$·93295
	,, = 0·157757	,,	$BaH_2O_28H_2O$	$\bar{1}$·19800
	,, = 0·098685	,,	$BaCO_3$	$\bar{2}$·99425
	,, = 0·02016	,,	MgO	$\bar{2}$·30449
	,, = 0·04216	,,	$MgCO_3$	$\bar{2}$·62490
	,, = 0·056108	,,	KHO	$\bar{2}$·74902
	,, = 0·0691	,,	K_2CO_3	$\bar{2}$·83948
	,, = 0·18814	,,	$KHC_4H_4O_6$	$\bar{1}$·27446
	,, = 0·108119	,,	$K_3C_6H_5O_7$, H_2O	$\bar{1}$·03390
	,, = 0·098124	,,	$KC_2H_3O_2$	$\bar{2}$·99178
	,, = 0·1411	,,	$KNaC_4H_4O_6$, $4H_2O$	$\bar{1}$·14952
	1 c.c. = 0·040008	,,	NaHO	$\bar{2}$·60215
	,, = 0·053	,,	Na_2CO_3	$\bar{2}$·72428
	,, = 0·14308	,,	$Na_2CO_310H_2O$	$\bar{1}$·15558
	,, = 0·084008	,,	$NaHCO_3$	$\bar{2}$·92432
Normal NaHO	1 c.c. = 0·040008	,,	NaHO	$\bar{2}$·60215
	,, = 0·031	,,	Na_2O	$\bar{2}$·49136
Normal KHO	1 c.c. = 0·056108	,,	KHO	$\bar{2}$·74902
	,, = 0·0471	,,	K_2O	$\bar{2}$·67302
Normal Na_2CO_3	1 c.c. = 0·053	,,	Na_2CO_3	$\bar{2}$·72428
	,, = 0·030	,,	CO_3	$\bar{2}$·47712
	,, = 0·022	,,	CO_2	$\bar{2}$·34242

		Coefficients.			Logarithms.
Normal Alkali	1 c.c.	= 0·060032	,,	$HC_2H_3O_2$	$\bar{2}$·77838
	,,	= 0·070027	,,	$H_3C_6H_5O_7H_2O$	$\bar{2}$·84527
	,,	= 0·036468	,,	HCl	$\bar{2}$·56191
	,,	= 0·080928	,,	HBr	$\bar{2}$·90810
	,,	= 0·012793	,,	HI	$\bar{1}$·10697
	,,	= 0·063018	,,	HNO_3	$\bar{2}$·79946
	,,	= 0·049038	,,	H_2SO_4	$\bar{2}$·69053
	,,	= 0·075024	,,	$H_2C_4H_4O_6$	$\bar{2}$·87520
N/10 Silver Nitrate	1 c.c.	= 0·010788	gm.	Ag	$\bar{2}$·03294
	,,	= 0·017	,,	$AgNO_3$	$\bar{2}$·23044
	,,	= 0·003546	,,	Cl	$\bar{3}$·54974
	,,	= 0·00535	,,	NH_4Cl	$\bar{3}$·72835
	,,	= 0·007456	,,	KCl	$\bar{3}$·87251
	,,	= 0·0119	,,	KBr	$\bar{2}$·07555
	,,	= 0·01029	,,	$NaBr$	$\bar{2}$·01242
	,,	= 0·0062	,,	Na_2HAsO_4	$\bar{3}$·79239
N/10 Iodine	1 c.c.	= 0·003203	,,	SO_2	$\bar{3}$·50555
	,,	= 0·004101	,,	H_2SO_3	$\bar{3}$·61321
	,,	= 0·004948	,,	As_2O_3	$\bar{3}$·69443
	,,	= 0·02482	,,	$Na_2S_2O_3 5H_2O$	$\bar{2}$·39480
	,,	= 0·012609	,,	$Na_2SO_3 7H_2O$	$\bar{2}$·10068
	,,	= 0·009714	,,	$K_2SO_3 2H_2O$	$\bar{3}$·98740
N/10 Dichromate	1 c.c.	= 0·01519	,,	$FeSO_4$	$\bar{2}$·18156
	,,	= 0·0278	,,	$FeSO_4 7H_2O$	$\bar{2}$·44404
	,,	= 0·011584	,,	$FeCO_3$	$\bar{2}$·06386
	,,	= 0·007184	,,	FeO	$\bar{3}$·85637
N/10 Thiosulphate	1 c.c.	= 0·02482	,,	Sodium thiosulphate	$\bar{2}$·39480
	,,	= 0·012692	,,	I	$\bar{2}$·10353
	,,	= 0·003546	,,	Cl	$\bar{3}$·54974
	,,	= 0·007992	,,	Br	$\bar{3}$·90266

CALCIUM (Ca = 40·07)	
1 c.c. N/10 permanganate = 0·0028035 ,, CaO	$\bar{3}$·44770
,, ,, = 0·0050035 ,, $CaCO_3$	$\bar{3}$·69927
,, ,, = 0·0086081 ,, $CaSO_4$, $2OH_2$	$\bar{3}$·93491
,, normal oxalic acid = 0·028035 ,, CaO	$\bar{2}$·44770
Cryst. oxalic acid × 0·444 = CaO	$\bar{1}$·64738
Ferrous ammonium sulphate × 0·07143 = CaO	$\bar{2}$·85388
CHLORINE (Cl = 35·46)	
1 c.c. N/10 silver solution = 0·003546 gm. Cl	$\bar{3}$·54974
= 0·005846 ,, $NaCl$	$\bar{3}$·76686
,, ,, arsenious or thiosulphate solution = 0·003546 gm. Cl	$\bar{3}$·54974
CHROMIUM (Cr = 52)	
Metallic iron × 0·3104 = Cr	$\bar{1}$·49192
,, × 0·5968 = CrO_3	$\bar{1}$·77586
,, × 0·878 = $K_2Cr_2O_7$	1·94347
,, × 1·929 = $PbCrO_4$	0·28540
Ferrous ammonium sulphate × 0·0443 = Cr	$\bar{2}$·64640
,, ,, × 0·0853 = CrO_3	$\bar{2}$·93095
,, ,, × 0·1253 = $K_2Cr_2O_7$	$\bar{1}$·09795
,, ,, × 0·2747 = $PbCrO_4$	$\bar{1}$·43891

Coefficients.	Logarithms.
1 c.c. N/10 solution = 0·003333 gm. CrO_3	3·52284
,, ,, = 0·004903 ,, $K_2Cr_2O_7$	3·69045
Copper (Cu = 63·57)	
1 c.c. N/10 solution = 0·006357 gm. Cu	$\bar{3}$·80325
Iron × 1·138 = copper	0·05614
Ferrous ammonium sulphate × 0·1622 = copper	$\bar{1}$·21005
Cyanogen (CN = 26·01)	
1 c.c. N/10 silver solution = 0·005202 gm. CN	3·71617
,, ,, = 0·005401 ,, HCN	3·73272
,, ,, = 0·013022 ,, KCN	2·11468
,, N/10 iodine = 0·003255 ,, KCN	3·51255
Potassium Ferrocyanide (K_4FeCy_6, $3OH_2$ = 422·348)	
Metallic iron × 7·563 = cryst. potassium ferrocyanide	0·87869
Ferrous ammonium sulphate × 1·080 = cryst. potassium ferrocyanide	0·03342
Potassium Ferricyanide ($K_6Fe_2Cy_{12}$ = 658·4)	
Metallic iron × 5·895 = potassium ferricyanide	0·77048
Ferrous ammonium sulphate × 1·684 = ,, ,,	0·22634
N/10 thiosulphate × 0·03292 = ,, ,,	$\bar{2}$·51746
Gold (Au = 197·2)	
1 c.c. normal oxalic acid = 0·0657 gm. gold	2·81757
Iodine (I = 126·92)	
1 c.c. N/10 thiosulphate = 0·012692 gm. iodine	2·10353
Iron (Fe = 55·84)	
1 c.c. N/10 permanganate, dichromate, or thiosulphate = 0·005584 Fe	3·74695
,, ,, ,, ,, = 0·007184 FeO	3·85637
,, ,, ,, ,, = 0·007984 Fe_2O_3	3·90222
Lead (Pb = 207·2)	
1 c.c. N/10 permanganate = 0·01036 gm. lead	$\bar{2}$·01536
1 c.c. normal oxalic acid = 0·1036 gm. lead	$\bar{1}$·61536
Metallic iron × 1·855 = lead	0·26841
Ferrous ammonium sulphate × 0·264 = lead	$\bar{1}$·42192
Manganese (Mn = 54·93) MnO = 70·93. MnO_2 = 86·93.	
Metallic iron × 0·4918 = Mn	1·69179
,, × 0·6350 = MnO	1·80277
,, × 0·7783 = MnO_2	1·89115
Ferrous ammonium sulphate × 0·0907 = MnO	$\bar{2}$·95761
,, ,, × 0·1112 = MnO_2	1·04610
Cryst. oxalic acid × 0·6896 = MnO_2	1·83860
1 c.c. N/10 solution = 0·003547 gm. MnO	3·54986
,, ,, = 0·004347 ,, MnO_2	3·63819
Mercury (Hg = 200·6)	
Ferrous ammonium sulphate × 0·5115 = Hg	1·70886
,, ,, × 0·6924 = $HgCl_2$	1·84033
1 c.c. N/10 solution = 0·02006 gm. Hg	2·30233
,, ,, = 0·02086 ,, Hg_2O	$\bar{2}$·31931
,, ,, = 0·027152 ,, $HgCl_2$	$\bar{2}$·43380
Nitrogen as Nitrates and Nitrites (N_2O_5 = 108·02. N_2O_3 = 76·02).	
Normal acid × 0·0510 = N_2O_5	$\bar{2}$·73239
,, × 0·1011 = KNO_3	$\bar{1}$·00475
Metallic iron × 0·3761 = HNO_3	1·57530
,, × 0·6035 = KNO_3	$\bar{1}$·78068
,, × 0·3224 = N_2O_5	1·50840
Silver (Ag = 107·88).	
1 c.c. N/10 NaCl = 0·010788 gm. Ag	$\bar{2}$·03294
,, ,, = 0·016989 ,, $AgNO_3$	$\bar{2}$·23017

Coefficients.	Logarithms.
SULPHURETTED HYDROGEN (H_2S = 34·076).	
1 c.c. N/10 arsenious solution = 0·002556 gm. H_2S	$\bar{3}$·40751
,, N/10 permanganate or iodine = 0·0017038 gm. H_2S	$\bar{3}$·23141
TIN (Sn = 118·7).	
Metallic iron × 1·063 = tin	0·02648
Ferrous ammonium sulphate × 0·1514 = tin	$\bar{1}$·17998
Factor for N/10 iodine or permanganate solution 0·005935	$\bar{3}$·77342
ZINC (Zn = 65·37).	
Metallic iron × 0·5852 = Zn	$\bar{1}$·76733
,, × 0·7285 = ZnO	$\bar{1}$·86241
Ferrous ammonium sulphate × 0·0836 = Zn	$\bar{2}$·92221
,, ,, × 0·1041 = ZnO	$\bar{1}$·01745
1 c.c. N/10 solution = 0·003268 gm. Zn	$\bar{3}$·51428

ADDENDA.

Page 35. **Modified Methyl Orange Indicator.**[1]—By the addition of an aniline dye to methyl orange the end-point of the indicator is considerably sharpened. Xylene cyanole FF (Sandoz' Chemical Co.) gave the best result when mixed in the proportion of 1·4 parts of the dye to 1 part of methyl orange. With the use of N/₁₀ acid and an alkaline liquid measuring about 50 c.c. the latter remained of a green colour to within 2 drops of the end-point, after which another drop produced a grey-green colour, and a further drop gave a colourless grey. Further addition of acid changed the colour of the solution to magenta. Good results were obtained in the titration of ammonia with HCl, and with phosphoric acid and NaOH, with the formation of the monosodium salt, but the indicator was useless with acetic acid. The new mixed indicator gives results with a 100 watt blue glass "daylight" lamp equal to those obtained by daylight.

Page 69. **Soda Ash, Caustic Soda, etc.**—The available alkali in commercial soda ash etc., is frequently expressed in terms of alkalimetric degrees, which are defined as follows:—

The French or Descroizilles degrees mean the quantity of real sulphuric acid, H_2SO_4, neutralized by 100 parts of soda ash.

The German degrees express the available alkali in terms of sodium carbonate Na_2CO_3. (Even the strength of caustic alkali is so expressed.)

Newcastle degrees (England) are calculated on the old equivalents for Na_2O and Na_2CO_3, viz. 32 and 59·26 respectively.

Usually 15·5 gm. of the alkali are dissolved in a 500 c.c. flask and made up to the mark. 50 c.c. of the well-mixed solution are then titrated with N/₁ HCl, using methyl orange as indicator. Each c.c. of standard acid used equals 2 per cent. of available alkali (Na_2O). The "degrees" are obtained as follows:—

Na_2O per cent. × 1·582 = French alkalimetric degrees
" " × 1·71 = German " "
" " × 1·013 = Newcastle " "
French degrees × 1·081 = German degrees
German degrees × 0·9252 = French degrees

(See Lunge's *Technical Chemists' Handbook*, p. 176 *et seq.*).

Page 371. **Formaldehyde. (Blank and Finkenberger's Method.)**—Measure 3 c.c. of the solution into a small weighed beaker with cover and weigh. Dilute and rinse the liquid into a 350 c.c. conical flask. Add 50 c.c. N/₁ soda, then 50 c.c. hydrogen peroxide solution (10 vol.), adding the latter slowly through a funnel. Cover the flask and allow to stand on top of a water-oven for 20-30 minutes. Then add litmus or phenolphthalein solution and titrate back with N/₁ sulphuric

[1] J. C. S. 1922, **121**, 2502-2506.

acid. 50 c.c. of the peroxide solution are then titrated with $N/_1$ soda, and the c.c. used deducted from the 50 c.c. of $N/_1$ soda added originally. From the difference subtract the c.c. of $N/_1$ sulphuric acid added, then the figure obtained multiplied by 2·979 and divided by the weight of the solution taken gives the percentage by weight of absolute formaldehyde. In the B.P. the solution should require for 3 c.c. from 36 to 38 c.c. of $N/_1$ soda, corresponding to 36-38 gm. of formaldehyde per 100 c.c.

Page 412. **Determination of Reducing Sugars by means of Fehling solution with Methylene Blue as internal indicator (J. H. Lane and L. Eynon[1]).**—This volumetric method is based on the long-known fact that in hot alkaline solutions methylene blue is reduced, i.e. decolorised, by aldoses and ketoses. It yields results as accurate as those given by the gravimetric Fehling method, and is unaffected by the presence of starch, proteins, suspended matter and substances retaining cuprous oxide in solution. The solutions employed are Fehling solution, prepared as described on p. 412, and a 1 per cent. solution of methylene blue in water. Maximum accuracy is attained by adhering to a consistent procedure. The indicator is so sensitive that the end-point can be determined in many cases to within one drop of the sugar solution, and it is always advisable to add the indicator only towards the end of the titration. A preliminary incremental titration is carried out by adding 15 c.c. of sugar solution to 10 or 25 c.c. of Fehling solution in a 300-400 c.c. flask and boiling the mixture for 15 seconds, when further 10 c.c. portions or less of the sugar solution are added, the liquid being boiled for 15 seconds between successive additions. When the copper is almost entirely reduced a few drops of the indicator are run in and the sugar solution is added in small increments, while ebullition is constantly maintained, until the methylene blue is decolorised. For many purposes this titration is sufficiently accurate (corrections are given whereby the error may be reduced to within 1 per cent.), but where maximum accuracy is desired the above titration is followed by another, carried out according to the standard procedure adopted by the authors as follows: To 10 or 25 c.c. of Fehling solution in a flask the sugar solution is added to within 0·5-1 c.c. of the amount required to complete the titration, and the mixture is boiled for 2 minutes. 3 to 5 drops of the indicator are then added, and the titration is completed in one minute, the liquid being maintained in continuous ebullition for the whole 3 minutes. The authors hold the burette in the hand over the flask, the burette being fitted with a small outlet tube bent twice at right angles. Burettes with glass taps are unsuitable, as the taps become heated by the steam and are liable to jam.

In the original paper (*loc. cit.*) Tables are given for use with the method both for 10 c.c. and 25 c.c. Fehling solution used, and for invert sugar (alone and in presence of sucrose), dextrose, lævulose, maltose, and lactose respectively. "Factors" are included in the tables representing the number of mgms. of sugar required to reduce the volume of Fehling solution used at the various concentrations, the factor for any given sugar varying appreciably with the concentration.

---

[1] *J. S. C. I.*, 1923, **42**, 32T.

Page 435. **Determination of Sugar in Urine by Lane and Eynon's method** (*supra*). -The urine, if acid, is rendered neutral to litmus, and then 20 c.c. is run from a burette into 10 c.c. of Fehling solution (Soxhlet's modification) in a 300 c.c. flask, and heated to boiling over a wire gauze. A trace of vaseline may be introduced into the liquid, to prevent excessive frothing. After 1 minute's actual ebullition 10 drops of a 1 per cent. solution of methylene blue are added. If this is completely decolorised within 15 seconds, so that the liquid appears exactly as before the addition, the urine contains more than 0·25 per cent. of reducers calculated as dextrose, and in that case it must be suitably diluted and titrated against Fehling solution by the method described above. If on the other hand, as is usually the case with normal urines, the methylene blue is not completely decolorised in about 15 seconds, the amount of reducers is less than 0·25 per cent., and should it be necessary to determine their amount the titration is continued by adding further quantities of the urine, 5 c.c. or 10 c.c. at a time, to the boiling liquid, giving about 15 seconds actual ebullition after each addition, until all trace of greenish tint has disappeared. For the determination of such small quantities of reducers 10 c.c. of Fehling solution may be taken as equivalent to 0·05 gm. of dextrose, but for the determination of very large amounts the special table (*loc. cit.*) should be used. The precision of the method increases with the amount of sugar to be determined, i.e with the degree of dilution of the urine employed for titration. The results agree closely with those given by Gerrard's cyano-cupric method, and are about 0·05-0·1 per cent. lower than those obtained by Pavy's method, a difference attributable to the reducing non-sugars, which affect Pavy's solution more than Fehling's. In the determination of very small quantities of sugar, the end-point of the titration may be made rather more distinct by first defecating the urine with neutral lead acetate and removing excess of lead by means of potassium oxalate, both of which reagents may be used in the dry state to avoid dilution. Methylene blue may be used as an internal indicator in Pavy's solution or Benedict's solution.

CORRIGENDA.

Page 48, line 4 from bottom.- For "$C_2H_4(COOH)_4$" read "$C_2H_4(COOH)_2$".

Page 336, line 7.- For "0·0092" read "9·2."

line 9. - For "0·0092" read "9·2."

line 10.- For "0·0094" read "9·4."

Page 458, line 4.--For "Table 7" read "Table VI."

Page 481, line 17. -After "Roscoe and Lunt's Table" read "(see Appendix, Table VII.)."

Page 481, line 6 from bottom. -For "Kers[illegible]" read "Kershaw."

INDEX TO PARTS I.-VIII.

(For List of Tables see Table of Contents.)

D = Determination.

ACETATE of lime, analysis of, 95.
Acetaldehyde, D. of, 374.
Acetic acid and acetates, titration of, 93.
— anhydride, D. of, 96.
Acetone, analysis of, 364.
Acetyl value of oils and fats, 398.
— — — — D. of, 398.
Acidimetry, 32.
Acid value (oils and fats), 388.
Aldehydes, various, D. of, 374.
Alkalimetry, 32.
Alkali carbonate and bicarbonate, D. of, in presence of each other, 64.
— chlorides, indirect D. of, 150
— hydroxides, D. of, in presence of small proportions of carbonates, 62.
— — — — small quantities of, in presence of carbonates, 63.
— salts, titration of, 59.
— — of organic acids, titration of, 68.
— — mixed caustic and carbonated, titration of, 67.
— sulphides, sulphites, thiosulphates and sulphates, D. of, 328.
Alkalies in presence of sulphites, D. of, 64.
— indirect D. of, 150.
Alkalimetry, 32.
Alkaline earths, D. of, 73.
— — indirect D. of, 149.
Alkalis, alkaline earths and acids, table for systematic analysis of, 59.
Alum cake, free acid in, 154.
Alumina cream, preparation of, 411.
Aluminium, D. of, 153.
Ammonia, D. of by distillation, 75.
— indirect D. of, 76.
— salts, analysis of, 75.
— semi-normal, 54.
Ammoniacal gas-liquor, analysis of, 77.
— liquors, analysis of, 79.
Ammonium-copper, normal solution of, 56.
— magnesium phosphate, titration of, 121.
— thiocyanate, decinormal, 151.
Aniline, D. of, 365.
Antimony, D. of, 156.
— titration with bromate, 160.
Argol, analysis of, 125.
Arsenic, D. of, 161.
— D. of as silver arsenate, 166.
— in iron ores, steel and pig iron, D. of, 169.
— in organic compounds, D. of, 172.
— in presence of tin, D. of, 163.
Arsenite, solution, decinormal, 144.
Arsenious acid, reaction with iodine,
— titration of, 144.
— sulphide, D. of, by iodine, 167.
Arsenite, $^{N}/_{10}$ solution of, 144.
Aurine, 39.
Azo-dyes, D. of, 367.
Azolitmin, 35.

BALANCE, the, 6.
Barium hydroxide, decinormal, 55.
— D. of, 172.
— thiosulphate, preparation and use of, 136.
Basic lead acetate, preparation of, 411.
Bifluorides, titration of, 118.
Bismuth, titration of, 173.
Black ash, analysis of, 79.
Bleaching powder, valuation of, 185.
Boric acid in butter, D. of, 100.
— — — milk and cream, D. of, 101.
— butter, etc., D. of, 99.
— — titration of, 97.
Bromates, D. of, 139.
Bromides, iodides and chlorides, D. of, 231.
Bromine value of oils and fats, 400.
— D. of, 139, 176.
Burette, the, 8.
— calibration of, 21.
— floats, 14.
Burettes, how to clean, 15.
— method of reading, 13.
— standardized, 13.
Butter, D. of Reichert-Wollny number of, 391, 395,

CADMIUM, D. of, 179.
Calcimeter, Scheibler's, 11[illegible]
Calcium, and magnesium, carbonates in waters, D. of, 74.
— — —, — etc., D. of, by Hehner's method, 459.
— — — — D. of, 180.
Calibration of graduated instruments, 18.
Cane-sugar, glucose and dextrin, D. of, 410, 416.
— inversion of, 410.
Carbolic acid, D. of, 404.
Carbon dioxide D. of, by volume, 108, 111.
— — in aerated waters, D. of, 107.
— — in air, D. of, 109.
— — in waters, D. of, 104.
— disulphide, D. of, 369.
— — in benzene, D. of, 370.
— in steel, colorimetric D. of (Eggertz) 248.
Carbonic acid, D. of, 101.
Caustic and carbonated alkalies, titration of, 61.
— potash or soda, D. of by dichromate, 65.
Cerium, D. of, 181
Chlorates, D. of, 186.
— indirect D. of, 140.
— iodates and bromates, D. of, 191.
Chloric and nitric acids, iodimetric D. of, 188.
Chloride of lime, titration of, 186.
Chlorides, bromides and iodides, D. of, 231.
— chlorates and perchlorates, analysis of mixtures of, 188.
— hypochlorites and chlorates, analysis of mixtures of, 186.
Chlorine, direct precipitation of, 183.
— titration of in neutral solution, 147.
— — — — acid solution (Volhard), 150, 184.
— water, titration of, 185.
Chromates, D. of, 140, 192.
Chrome iron ore, analysis of, 193.
Chromic acid, iodimetric D. of, 192, 199.
Chorley's apparatus for preserving standard solutions, 24.
Chromium, reduction by iron, 192.
— in steel, D. of, 196, 198, 352.
Citric acid, D. of, 114.
Cobalt, D. of, 200.
Cochineal solution, 38.
Congo red, 39.
Copper, D. of, 201.
— — as cuprous iodide, 203.
— — as cuprous thiocyanate (Volhard), 210.
— — as sulphide (Pelouze), 208.
— — by potassium cyanide (Parkes), 206.
— — by stannous chloride (Weil), 209.
— — by titration of copper ferrocyanide (Sanchez), 217.
Copper and iron, D. of, 210.
— colorimetric D. of, 215.
— in water supplies, D. of, 256.
— ores, Steinbeck's process for, 212.
Corallin, 39.
Cream of tartar, analysis of, 121.
Cresols, D. of, 404.
Cyanides used in gold extraction, analysis of, 21[illegible].
Cyanogen, titration of, 218.
— mud, 225.

DEXTRIN, D. of, 416.
Dichromates, D. of, 140.
Distillation of substances with hydrochloric acid into alkali iodide, 140.

ERYTHROSIN, 41.
Ester value of oils and fats, 391.
Ethyl orange, 36.

FACTORS for the calculation of analyses, 31.
Fats, analysis of, 387.
Fehling's solution, preparation of, 412.
Ferric compounds, reduction to ferrous, 1[illegible]3, 239.
— — titration of, 240.
— indicator for Volhard's process, 151
Ferricyanides, titration of, 225
Ferrochrome, 196.
Ferrocyanides, analysis of, 220, 221.
— commercial, analysis of, 222.
Flasks, Giles's, 17.
— measuring, 16.
Float, Erdmann's, 14.
Formaldehyde, D. of, 371, 623.
Formalin, 371.
Formic acid, D. of, 115.
Friedrich's glass stop-cock, 12.
Fruit juices, D. of citric acid in, 115.

GAS liquor, analysis of, 77.
Geissler's burette, 10.
Glass stop-cocks, lubricant for, 15.
Glucose, D. of (Fehling), 412.
— — — by cyano-cupric process (Gerrard), 415.
— — — — Pavy's method, 413.
— sucrose and dextrin, D. of, 416.
Glycerin (crude), international methods for analysis of, 376.
Glycerol, D. of, 375.
— in oils and fats, D. of, 383.
Gold, D. of, 228.
Graduated instruments, the correct reading of, 13.

HARDNESS of waters, Hehner's method for D. of, 459.
Hehner value of oils and fats, 388.

Herzfeld's method for D. of sucrose, 410.
Hofmann's clamp, 11.
Hydrofluoric acid, D. of, 116.
Hydrofluosilicic acid, D. of, 118.
Hydrogen peroxide, analysis of, 304.
Hydroxides and carbonates, mixed, D. of, 61.
Hydroxyl, analysis of, 304.
Hypophosphites, D. of, 317.

INDICATORS, 32.
— application of ionic theory to, 44.
— classification of, 40.
— extra sensitive, 41.
— general characteristics of,
— sensitiveness of, 32.
— theory of, 41.
— Thomson's results with, 40.
— use of two, 33, 62.
Indicator, ferric, 151.
Indigo, red in indigo, D. of, 387.
— valuation of, 382.
Indirect determination of ammonia, lime, alkaline earths, etc., 149.
Iodates, D. of, 139.
Iodides, bromides and chlorides, D. of, 231.
— influence of in iodimetry, 137.
— titration of with decinormal silver, 236, 318.
Iodine, D. by distillation, 229.
— combined, oxidation by chlorine, 233.
— — — in presence of bromides and chlorides, 231.
— free, titration of, 134.
— titrations, cause of re-appearance of blue colour, 135.
— value of oils and fats, 400.
— — — D. of, 400.
Iodimetry and iodimetric processes, 134.
— decinormal solution of, 136.
— oxidation by permanganate, 234.
Iron, colorimetric D. of, 244.
— D. of in pharmaceutical syrups, 240.
— in water, D. of, 245.
— (ferric), D. with iodine and thiosulphate, 243.
— — reduction to ferrous state, 239.
— — titration by sodium thiosulphate, 242.
— — — permanganate, 131.
— — — stannous chloride, 289.
— — — titanous chloride, 240.
— (ferrous), titration with dichromate (Penny), 132, 236.
— — — with permanganate, 237.
— ores, analysis of, 246.

KJELDAHL's method for nitrogen, 85.
Kjeldahl-Gunning process, 86.
— Jodlbauer process, 91.
Köttstorfer value of oils and fats, 389.

LACMOID, 39.
Lactose, D. of, [illegible].
Lead, D. of, 252.
— dioxide, D. of, 140.
— in citric and tartaric acids, D. of, 254.
— — cream of tartar, D. of, 254.
— — presence of iron, colorimetric D. of, 257.
— — waters, colorimetric D. of, 256.
— — — permissible amount of, 257.
— and zinc, D. of, 360.
Leffmann and Beam's modification of Reichert process for butter, 396.
Lime and lemon juices, D. of citric acid in, 115.
Litmus paper, 35.
— solution, 33.
— theory of the action of, 35.
Litre, the, 25.

Magnesium, D. of, 258.
— in waters, D. of, 259.
Manganese, D. of, 260.
— — by bismuthate process, 266.
— — — iron, 272.
— — — permanganate (Volhard), 265, 266.
— — — persulphate, 269.
— colorimetric D. of small quantities of, in water (Luhrig), 269.
— dioxide, valuation of, 270.
— ores, technical examination of, 270.
Measuring flask, the, 16.
— — calibration of, 19.
Mercury, D. of, 273.
Methyl orange, 35, 623.
— red, 36.
— salicylate, analysis of, 408.
Methylene blue indicator, 138.
Metric system, the, 24.
Milk-sugar, D. of, 416.
— and cane-sugar, D. of, 416.
Mohr's burette, 8.
— — mode of using, 11.
Molybdate solution (Pemberton), 313.

NESSLER's solution, 486.
Nickel, D. of, 278.
— and cobalt, D. by ferrocyanide, [illegible].
— — — — cyanide, 284.
— in steel, D. of, 281, 283.
— rapid D. in presence of chromium, iron, and manganese, 282.
Nitrate of lime, indirect D. of nitrogen in, 74.
Nitrates, D. by conversion into ammonia (Schulze), 285.
— — — — (Devarda's method), 299.
— — as nitric oxide (Crum), 449.
— — by Kjeldahl-Gunning-Jodlbauer process, 91.

Nitrates, D. by oxidation of ferrous salts (Pelouze), 287.
— — — — — (Schlösing), 291.
— — — in the absence of ammonium salts (Ulsch), 297.
— — — — — — and of organic nitrogen, 298.
Nitric acid, iodimetric D. of, 189.
— and nitrous acids, separate D. of (Frankland), 304.
Nitrites, D. by permanganate, 303.
— gasometric D. of, 303.
— iodimetric D. of, 300.
Nitrogen in the absence of nitrates, D. of, 86.
— — — presence of nitrates, D. of, 9[illegible].
— D. by Ronchèse's method, 93.
— in spent oxide, D. of, 92.
— — nitro-substitution compounds, D. of, 92.
Nordhausen sulphuric acid, analysis of, 122.
Normal acid and alkali solutions, preparation of, 45.
— hydrochloric acid, 53.
— nitric acid, 53.
— oxalic acid, 51.
— potash and soda, 54.
— potassium carbonate, 49.
— sodium carbonate, 49.
— solution, definition of, 29.
— sulphuric acid, 49.

Oils, analysis of, 387.
Oleum, 122.
Organic salts of the alkalies, titration of, 68.
Oxalic acid, titration of, 120.
Oxidizing agents used in volumetric analysis, 127.
Oxygen dissolved, D. of, 468.
— — in waters and effluents, D. of, 468, 480.
— — iodimetric D. of (Thresh), 475.

Pavy's solution, 413.
Pemberton's molybdic method for D. of phosphoric acid, 313.
Perchlorate in Chili saltpetre, D. of, 188.
Persulphates, D. of, 342.
Phenacetolin, 38.
Phenolphthalein, 37.
— and methyl orange, mixture of, 38.
— behaviour with boric acid, 97.
Phenols, D. of, 404.
Phosphates, D. by uranium solution, 307.
— — — silver nitrate (Holleman), 316.
Phosphites, iodimetric D. of, 317.
Phosphoric acid in combination with lime and magnesia, D. of, 310.
— — — alkali and alkaline earthy phosphates, D. of, 313.
— — — foodstuffs, D. of, 316.
— — D. by silver nitrate, 316.
Phosphoric acid, titration of, [illegible]0.
Phosphorus in iron and steel, D. of, 249.
Pinch-cocks, 11.
Pipette, the, 15.
— calibration of, 20.
Polenske value of fats, D. of, 397.
Potassium and sodium chlorides, indirect D. of, 150.
— bi-iodate as standardizing reagent, 48.
— D. by sodium cobaltinitrite, 68.
— dichromate, decinormal solution of, 134.
— ferrocyanide, titration of, 220.
— iodate, use of in iodimetry, 138.
— permanganate, decinormal solution of, 128.
— — — — — — calculation of results of analyses made with, 131.
— tetroxalate as standardizing reagent, 55.
— thiocyanate, decinormal, 151.
Preservation of standard solutions, 22.

Reducing agents used in volumetric analysis, 128.
Reichert value of oils and fats, 391.
Reichert-Meissl and Reichert-Wollny value, D. of, 391.
Residual method of analysis, 4.
Rosolic acid, 39.

Salicylic acid, D. of, 406.
— — limits of, allowed in food, 408.
Salt cake, analysis of, 70.
Saponification value of oils and fats, 389.
Schellbach's burette, 9.
Selenium, D. of, 318.
Sewage, analysis of, 444.
— effluents, standards for, 484.
— — typical analyses of, 486.
Silver, D. by decinormal sodium chloride, 318.
— in acid solution, D. of (Volhard), 150, 319.
— — ores and alloys, D. of, 319.
— — plate, coin, etc., D. of, 320.
— solution, decinormal, 146.
Soap, analysis of, 71.
Soda ash, analysis of, 69, 623.
Sodium, D. by potassium dihydroxytartrate and permanganate, 65.
— carbonate as standardizing re-agent, 46.
— chloride, decinormal solution of, 147.
— oxalate as standardizing reagent, 48.
— perborate, 306.
— peroxide, analysis of 306.
— silicate, titration of, 37.
— thiosulphate and iodine, reaction between, 135.
— — decinormal solution of, 136.
— — as standard in alkalimetry, 47.
— — Volhard's method of standardization, 401.

Spent liquor, ammoniacal, analysis of, 7[illegible].
— oxide, 225.
Standard solutions, adjustment of, 56.
— — corrections for temperature, 26, 28.
Stannous chloride solution, preparation of, 134.
Starch, D. of, 417.
— indicator, preparation of, 1[illegible]7.
— paper, iodized, 145.
Steel, sulphur in, 333.
Sugar solutions, clarification of, 411.
Sugars, 409.
— conversion into glucose, 410.
— D. by cyano-cupric process, 415.
— reducing, D. of, 412.
Sulphides, alkali, D. of, 327.
Sulphocyanides. *See* Thiocyanates.
Sulphur in coal-gas, D. of, 325.
— — iron and steel, D. of, 250, 333.
— — pyrites, etc., D. of, 324.
— — sulphides, D. of, 326.
Sulphuretted hydrogen, D. of, 334.
Sulphuric acid, D. of, 336.
— — fuming, analysis of, 122.
Sulphurous acid and sulphites, D. of, 327.
Superphosphate, D. of phosphoric acid in, 3[illegible]2.

TANNIC acid, D. of, 419, 424.
Tannin in hops, D. of, 423.
— — tea, D. of, 421.
— — wine, cider, etc., D. of, 423.
— materials, rapid method for, 426.
— precipitation by gelatin, 427.
Tartaric acid, titration of, 1[illegible].
Tartrates, analysis of, 124.
Test-mixers, 18.
Thiocarbonates, D. of, 369.
Thiocyanates, D. of, 2[illegible]6.
— — — (Volhard), 150.
Tin, colorimetric D. in foodstuffs, 346.
— D. of, 343.
— in white-metal alloys, D. of, 345.
— ore, analysis of, 345.
— (stannous), titration by ferric chloride, 344.
Titanium, D. of, 348.
Titanous chloride, standard solution of, 240
Titration, direct and indirect, 4.
— of hot solutions, 12.
Titration, residual, 4.
Tolerances of graduated burettes, 2[illegible].
— — — cylinders, 22.
— — — pipettes, 21.
— — — flasks, 19.
Turmeric paper, 38.
Thiosulphate in presence of sulphide, sulphite, and bisulphite, D. of, 332.

URANIUM, D. of, 350.
Urea, D. of, 430.
Urine, analysis 428.
— — D. of albumen in, 442.
— — — ammonia in, 440.
— — — chlorides in, 429.
— — — free acid in, 442.
— — — glucose in, 435.
— — — lime and magnesia in, 439
— — — phosphoric acid in, 433.
— — — soda and potash in, 443.
— — — sulphuric acid in, 434.
— — — total nitrogen in, 443.
— — — uric acid in, 435.

VANADIUM, D. of, 351.
— in steel, D. of, 352.
Vinegar, D. of free mineral acids in, 94.
Volumetric analysis without weights, 6.
— — — burettes, 7.

WATER analysis, Special Index of Processes, 444.
— — preparation of reagents for, 486.
Waters, analysis of, 441.
Waxes, analysis of, 387.
Weights and measures used in volumetric analysis, 24.
Wijs' solution of iodine, 103.

ZINC dust, analysis of, 361.
— and lead, D. of, 360.
— — manganese, D. of, 387.
— D. as ferrocyanide, 355.
— — — phosphate, 359.
— — — zinc-mercury thiocyanate, 359.
— in blende, D. of, 351.
— in water supplies, D. of, 256.
— precipitation as sulphide, etc., 353.
— oxide and carbonate, titration of, 363.

PRINTED IN GREAT BRITAIN AT THE UNIVERSITY PRESS, ABERDEEN

NOTES.

NOTES.

NOTES.